



Atomic Energy
Control Board

Commission de contrôle
de l'énergie atomique

P.O. Box 1046
Ottawa, Canada
K1P 5S9

C.P. 1046
Ottawa, Canada
K1P 5S9

INFO-0118

CORROSION OF STEELS IN
SOUR GAS ENVIRONMENTS

by

R.J. Twigg, P. Eng.
Glencor Engineering Ltd.

A research report prepared for the
Atomic Energy Control Board
Ottawa, Canada

RESEARCH REPORT

March 1984

CORROSION OF STEELS IN
SOUR GAS ENVIRONMENTS

A report prepared by Glencor Engineering Limited, under contract to the Atomic Energy Control Board.

ABSTRACT

This report presents a study on the effects of sour gas environments on steels. Emphasis is placed on alloys commonly used in the Heavy Water, Sour Gas and Refining Industries. In addition, "high strength, low alloy" steels, known as "oil country tubular goods", are included. Reference is made to the effects of hydrogen sulphide environments on austenitic steels and on certain specialty steels.

Theories of hydrogen-related cracking mechanisms are outlined with emphasis placed on Sulphide Stress Cracking and Hydrogen Induced Cracking in carbon and low alloy steels.

Methods of controlling Sulphide Stress Cracking and Hydrogen Induced Cracking are addressed separately.

Case histories from the Heavy Water, Refining, and Sour Gas Industries are used to illustrate operating experience and failure mechanisms.

Finally, recommendations, based largely on the author's industrial experience, are made with respect to Quality Assurance and Inspection requirements for sour service components.

Only published literature was surveyed. Abstracts were made of all references, reviewing the major sources in detail.

DISCLAIMER

The Atomic Energy Control Board is not responsible for the accuracy of the statements made or opinions expressed in this publication and neither the Board nor the author assumes liability with respect to any damage or loss incurred as a result of the use made of the information contained in this publication.

RÉSUMÉ

Le présent rapport fournit les résultats d'une étude sur les effets des milieux gazeux acides sur les aciers. On a surtout examiné attentivement les aciers utilisés dans les usines d'eau lourde, les raffineries de pétrole et les installations utilisant des gaz acides. De plus, le rapport comprend des données sur les aciers "faiblement alliés de grande résistance", communément appelés "fournitures tubulaires pour puits de pétrole". On y fait aussi mention des effets de l'hydrogène sulfuré sur les aciers austénitiques et sur certains aciers spéciaux.

Les théories sur la fissuration en présence d'hydrogène sont décrites en insistant sur les mécanismes de fissuration sous contrainte par le sulfure et de fissuration causée par l'hydrogène proprement dit dans les aciers au carbone et faiblement alliés.

Les méthodes pour contrôler la fissuration sous contrainte par le sulfure et celle causée par l'hydrogène proprement dit sont discutées séparément.

Des cas concrets tirés des industries d'eau lourde, des raffineries de pétrole et des installations utilisant des gaz acides, servent à illustrer ce qui peut arriver en cours de fonctionnement et comment peuvent se produire les défaillances.

Finalement, le rapport offre certaines recommandations concernant les exigences d'assurance-qualité et d'inspection des composants utilisés en milieu gazeux acide. Ces recommandations sont basées, en grande partie, sur l'expérience pratique de l'auteur dans le domaine industriel.

Seuls les ouvrages publiés ont été consultés. Des résumés des textes de référence ont été préparés et les sources importantes ont été examinées plus profondément.

ACKNOWLEDGEMENTS

The author would like to thank personnel of Shell Canada Limited, Shell Canada Resources Limited, and Gulf Canada Resources Limited for helpful discussions concerning materials, field experience and inspection techniques. Special thanks are extended to M.G. Hay of Shell Canada Limited for identifying additional sources of information and outlining his relevant testing experience. In addition, R.C. Carlson of Gulf Canada Resources Limited provided information from both his extensive background in the Sour Gas Industry and his chairmanship of the CSA Task Force on the Cracking of Pipeline Steels.

G.J. Biefer of Canmet, G.F. Taylor of Chalk River Nuclear Laboratories, and A. Ikeda of Sumitomo Metals also helped by supplying papers for the study.

Finally, the author would like to express his appreciation to Dr. A. Omar of the Atomic Energy Control Board for his guidance in preparing the report.

TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT and DISCLAIMER	i
RÉSUMÉ	ii
ACKNOWLEDGEMENTS	iii
1. SCOPE OF WORK	1
2. GLOSSARY OF TERMS	2
3. SOUR SERVICE ENVIRONMENTS	6
3.1 Heavy Water Industry	6
3.2 Sour Gas Industry	7
3.3 Refineries	7
4. EFFECTS OF HYDROGEN SULPHIDE ON STEEL	8
4.1 Hydrogen Cracking Mechanism	8
5. THEORIES OF HYDROGEN DAMAGE	10
5.1 Precipitation of Molecular Hydrogen in Microvoids	10
5.2 Decohesion Theory	10
5.3 Theory of Brittle Fracture	10
5.4 Hydrogen Wetting Theory	10
5.5 Dislocation Mobility Theory	11
5.6 Summary	11
6. CORROSION OF ALLOYS BY HYDROGEN SULPHIDE	12
6.1 Carbon Steels	12
6.2 High Alloys including Austenitic Stainless Steels	17
6.3 Summary	19
7. SULPHIDE STRESS CRACKING	21
7.1 Microstructure	22
7.2 Alloying Elements	22
7.3 Crack Morphology	24
7.4 Other Environmental Variables	24
7.5 Summary	25
Table 7.1 - Sulphide Stress Corrosion Cracking Failures	27
8. HYDROGEN INDUCED CRACKING (HIC)	29
8.1 Cracking Morphology	30
8.2 Environmental Variables	31
8.3 Metallurgical Variables	32
8.4 Measuring the Effects of Hydrogen Induced Cracking Upon Service Life	37
8.5 Summary	39
Table 8.1 - Hydrogen Damage Resistance Requirements for Hydrogen Sulphide Service	41
Table 8.2 - Several Examples of Failure by Hydrogen Induced Cracking ..	42
Figure 8.1 - Schematic of HIC under Heavy Water Plant Conditions	43
Figure 8.2 - Hydrogen Concentration in Through-Thickness Direction in Standard and One-Side Exposed HIC Specimens	44
Figure 8.3 - Factors Affecting Hydrogen Sulphide Induced Cracking	45

9. TEST METHODS	46
9.1 Static Bend Test (SSC)	46
9.2 C-Ring (SSC)	46
9.3 Bent Beam Test (SSC)	47
9.4 Double Cantilever Beam (SSC)	48
9.5 Slow Strain Rate (SSC)	49
9.6 Hydrogen Induced Cracking (HIC)	49
Table 9.1 - Test Solutions	51
10. CASE HISTORIES	52
10.1 Heavy Water Industry	52
10.2 Sour Gas Industry	53
10.3 Refining Industry	57
10.4 Summary	59
11. MATERIALS OF CONSTRUCTION	60
11.1 Alloys Resistant to Sulphide Stress Cracking	61
11.2 Valves	61
11.3 Sour Service Bolting	61
11.4 Summary	62
12. INSPECTION AND QUALITY CONTROL	63
12.1 New Components	63
12.2 Plant Program	66
12.3 Inhibition Program	71
12.4 Repair Welding	71
12.5 Summary	72
Table 12.1 - Piping Corrosion Survey Sheet	73
13. SPECIFICATIONS USED FOR SOUR SERVICE	74
13.1 NACE-MR-01-75	74
13.2 NACE MR-01-76	74
13.3 NACE TM-01-77	74
13.4 Proposed NACE Test Method for Elastomerics	75
13.5 Step-Wise Cracking Test	75
14. SUMMARY OF REPORT	76
14.1 Environmental Parameters	76
14.2 Metallurgical Parameters	77
14.3 Corrosion	78
14.4 Corrosion Inhibitors	78
14.5 Quality Assurance	79
PHOTOGRAPHS	80
COMMENTS ON REFERENCES	APPENDIX A
REFERENCES	APPENDIX B

CORROSION OF STEELS IN sour GAS ENVIRONMENTS

1. SCOPE OF WORK

A critical review of literature was undertaken with respect to the effects of hydrogen sulphide environments upon steels, low alloy, and high alloy materials, both in laboratory and process situations. The purpose of the review was to establish:

- (a) conditions leading to failure,
- (b) theories pertaining to failure mechanisms,
- (c) methods and materials used to prevent failures,
- (d) inspection and/or monitoring techniques that may be used to detect potential failures, and
- (e) case histories outlining operating experience with materials in sour environments.

2. GLOSSARY OF TERMS

These definitions are abstracted from the National Association of Corrosion Engineers' (NACE) Glossary of Corrosion Related Terms. The only exception involves the terminology for Hydrogen Induced Cracking assessment. This was derived from procedures established by the Sour Gas and Heavy Water Industries.

Anion: A negatively charged ion of an electrolyte which migrates toward the anode under the influence of a potential gradient.

Anode: The electrode of an electrolytic cell at which oxidation occurs.

Anodic Inhibitor: A chemical substance or mixture that prevents or reduces the rate of the anodic, or oxidation, reaction.

Austenite: A face-centered cubic crystalline phase of iron-base alloys.

Cathode: The electrode of an electrolytic cell at which reduction occurs.

Cathodic Inhibitor: A chemical substance, or mixture, that either prevents or reduces the rate of cathodic, or reduction, reaction.

Cation: A positively charged ion of an electrolyte which migrates toward the cathode under the influence of a potential gradient.

Corrosion Potential (E_{corr}): The potential of a corroding surface in an electrolyte relative to a reference electrode.

Embrittlement: Severe loss of ductility of a material due to chemical or physical changes.

Ferrite: A body-centered cubic crystalline phase of iron-base alloys.

Fracture Mechanics: A quantitative analysis for evaluating structural reliability in terms of applied stress, crack length, and specimen geometry.

Galvanic Corrosion: Corrosion associated with the current resulting from the electrical coupling of dissimilar electrodes in an electrolyte.

General Corrosion: A form of deterioration that is distributed more or less uniformly over a surface.

Heat Affected Zone (HAZ): That portion of the base metal that was not melted during cutting or welding, but whose microstructure and properties have been altered by the heat of the process.

Hydrogen Blistering: Subsurface voids produced by hydrogen absorption in (usually) low strength alloys, resulting in surface bulges. Blisters are associated with non-metallic inclusions and defects such as laminations in the material.

Hydrogen Embrittlement (HE): A loss of ductility in metals resulting from the absorption of hydrogen.

Hydrogen Stress Cracking: A failure process that results from the initial presence or absorption of hydrogen in metals in combination with residual or applied tensile stresses. It occurs most frequently with high strength alloys. The cracks generally occur at right angles to the stress direction.

Intergranular Corrosion: Preferential corrosion at grain boundaries of a metal or alloy.

K_{ISCC}: Abbreviation for the critical value of the plane strain stress intensity factor which will just produce crack propagation by stress corrosion cracking of a given material in a given environment.

Martensite: A supersaturated solid solution of carbon in iron characterized by an acicular (needle-like) microstructure.

Normalizing: Heating a ferrous alloy to a suitable temperature above the transformation range (austenitizing), holding it at temperature for a suitable time, and then cooling it in still air to a temperature substantially below the transformation range.

Precipitation Hardening: Hardening caused by the precipitation of a constituent from a supersaturated solid solution.

Sensitizing Heat Treatment: A heat treatment, whether accidental, intentional, or incidental (during welding), which causes precipitation of constituents at grain boundaries, often causing the alloy to become susceptible to intergranular corrosion or to intergranular stress corrosion cracking.

Slow Strain Rate Technique: An experimental technique of evaluating susceptibility to stress corrosion cracking. It involves pulling a specimen to failure in uniaxial tension at a controlled slow strain rate while the specimen is in the test environment, and examining the specimen for evidence of stress corrosion cracking.

Solution Heat Treatment: Heating a metal to a suitable temperature and holding at that temperature long enough for one or more constituents to enter into solid solution and then cooling rapidly enough to retain the constituents in solution.

Stress Corrosion Cracking (SCC): Cracking of metals produced by the combined action of corrosion and tensile stress (residual or applied).

Sulphide Stress Cracking (SSC): Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulphide. The cracks occur at right angles to the stress direction.

Hydrogen Induced Cracking Terminology:

Crack Length Ratio (CLR)

$$\frac{\text{sum of the lengths of all lengthwise and step-wise cracks}}{\text{number of cross-sections examined (9) x specimen width}} \times 100$$

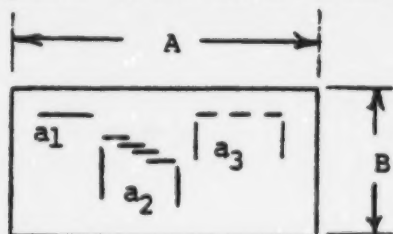
Crack Thickness Ratio (CTR):

$$\frac{\text{sum of the thicknesses of all step-wise cracks} \times 100}{\text{number of cross-sections examined (9)} \times \text{specimen thickness}}$$

Crack Sensitivity Ratio (CSR):

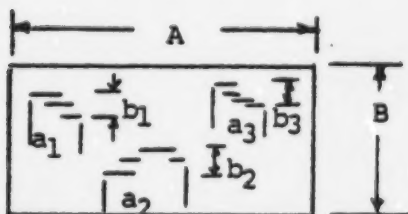
$$\frac{\text{sum of the step-wise crack area} \times 100}{\text{number of cross sections examined (9)} \times \text{specimen area}}$$

(Convention requires that 9 cross sections be examined per test.)



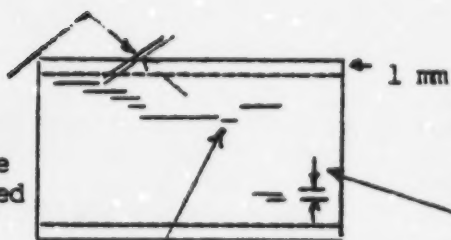
$$CLR = \frac{\sum a \times 100}{9A}$$

$$CTR = \frac{\sum b \times 100}{9B}$$



$$CSR = \frac{\sum a.b \times 100}{9(A \times B)}$$

Cracks over 0.5 mm from the nearest crack end are not considered as the same step-wise crack.



When crack length is 0.1 mm or shorter, it is not considered a step-wise crack.

This part is disregarded - i.e. any cracks within 1 mm of surface are ignored unless they extend more than 1 mm into sample.

If this distance is less than 0.5 mm crack is not considered as step-wise.

Crack Morphology in Wet Hydrogen Sulphide Environments

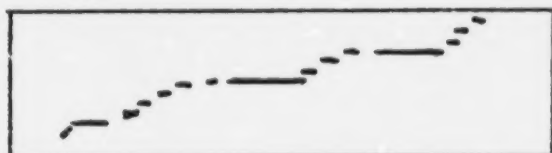
(After Ikeda and Kowaka, Reference 154)



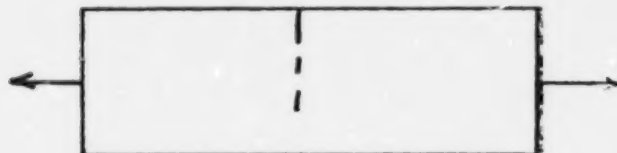
Blistering



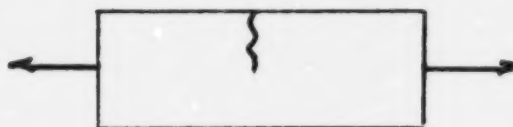
Blistering, HIC and SSC



HIC with SSC



SSC in low strength steel



SSC in high strength steel

(arrows indicate direction of applied stress)

3. SOUR SERVICE ENVIRONMENTS

Sour service can be considered any service involving water and hydrogen sulphide. However, the NACE defines a sour gas environment as any system containing H₂S at a partial pressure greater than 0.34 kPa (0.05 psia), or 11.3 ppm, and operating at a total pressure above 448 kPa (65 psia) (Ref. 1).

This definition is considered too liberal by some as cracking has been experienced in solutions with 0.5% acetic acid at H₂S concentrations of less than 3.4 ppm (Ref. 4,30) and 2 ppm (Ref. 59). In addition, tests involving acidified brine have produced cracks at hydrogen sulphide concentrations as low as 1 ppm (Ref. 163). Consequently, the Canadian Sour Gas Industry defines as sour any environment containing hydrogen sulphide.

Definitions can be misleading as the remaining composition of the environment may be equally important. Cracking was found to cease in environments with a pH above 9.5 even in the presence of a considerable concentration of hydrogen sulphide (Ref. 25). Similarly, absorption of hydrogen sulphide by the materials used to construct the test apparatus can lead to low concentration indications when, in reality, cracking could occur.

Sour oil and multiphase systems can also present problems. These systems, containing H₂S, are defined as sour by the NACE (Ref. 1) when:

- (a) the maximum gas/liquid ratio is above 0.88 cubic metres of gas/litre of liquid (5000 SCF/barrel);
- (b) the gas phase contains more than 1% H₂S;
- (c) the partial pressure of H₂S in the gas phase exceeds 69 kPa (10 psia);
and
- (d) the surface operating pressure exceeds 1.8 MPa (265 psia).

Higher pressures are accepted in these systems since it is generally felt that the presence of oil reduces corrosion, and subsequent cracking, by forming an inhibiting film on the surface of the metal. However, studies have revealed that under sour conditions oil does not display the inhibitive properties attributed to it (Ref. 35).

Moist hydrogen sulphide is the primary source of corrosion in a sour gas environment. The presence of contaminating species such as chlorides and carbon dioxide contributes to the aggressiveness of the environment.

3.1 Heavy Water Industry

The Heavy Water Industry identifies as sour, any service containing detectable quantities of hydrogen sulphide. To avoid brittle fracture, design specifications for pressure-containing components generally require materials listed in NACE MR-01-75.

Operating temperatures of heavy water plants are typically 30°-150°C with pressures of 310 kPa - 3.1 MPa (45-450 psi). The environment is either moist hydrogen sulphide gas or a gaseous-aqueous, hydrogen sulphide mixture (Ref. 10,81,97,98,101,142,143,174). When carbon and low alloy steels are initially exposed to this medium, corrosion rates are high, often reaching 25 mm per year (Ref. 83,174). In time, corrosion products and scales form on the steel surface. Under certain conditions, these scales become protective, reducing the rate of corrosion to manageable levels (Ref. 10,83,98,101,142,174).

To prevent erosion of a stable sulphide scale on a steel surface, stream velocities must be limited. Design parameters limit gas velocities to less than 18 metres/second and liquid velocities to less than 2.1 metres/second (Ref. 83, 85,91,174).

3.2 Sour Gas Industry

The environment involved in the sour gas industry is quite complex. It can include CO₂, various chlorides and only trace amounts of H₂S. On the other hand, the gas may contain up to 70% H₂S.

In addition, inhibitors, used in the gas-gathering systems and down the wells to prevent corrosion, will reduce the sulphide effect. However, severe corrosion, cracking, and blistering can still occur where wet conditions exist, particularly in low sections of the gas lines and in sulfinol contactors (Ref. 7,12,56,73,138).

3.3 Refineries

Refineries encounter sour environments under two separate sets of conditions.

One type of refinery environment involves hydrogen sulphide in crude oil. As in the sour gas industry, H₂S levels vary widely. Hydrogen blistering has occurred in crude oil storage tanks where a water phase exists, normally in the bottom of the tank or just under the roof. Crude oil pipeline failure due to H₂S is not common but it has been documented (Ref. 175).

The second, and more commonly experienced, sour environment in refineries involves ammonia in the in-going stream at a pH of 7-9 (Ref. 33,37,39,40) and hydrogen sulphide-containing condensate in the hydrocracker effluent (Ref. 47). Small amounts of the ammonia may convert to cyanide or hydrogen cyanide which promotes entry of hydrogen into steel. The resulting damage is identical to that occurring at lower pH in gas plants.

Lowering or raising the pH can reduce the cyanide effect. Air or polysulphide injections also are used to control the cyanide attack, thereby limiting hydrogen sulphide damage (Ref. 33,35,37,38,39,40).

4. EFFECTS OF HYDROGEN SULPHIDE ON STEEL

The effects of hydrogen sulphide on carbon and low alloy steels go by many names and these have led to confusion in the industry. These effects have been termed:

- (a) Sulphide Stress Corrosion Cracking (SSCC)
- (b) Sulphide, Hydrogen Stress Corrosion Cracking (SHSCC)
- (c) Hydrogen Pressure Cracking (HPC)
- (d) Hydrogen Assisted Cracking (HAC)
- (e) Hydrogen Environment Cracking (HEC)
- (f) Hydrogen Induced Cracking (HIC)
- (g) Hydrogen Induced Step-Wise Cracking (HSWC)
- (h) Hydrogen Blister Cracking (HBC)
- (i) Sulphide Stress Cracking (SSC)
- (j) Sulphide Cracking (SC)
- (k) Blistering
- (l) Blister Cracking

Confusion in describing H₂S attack on steels arises from the fact that, although a hydrogen cracking mechanism appears to be responsible in all cases, low strength steels tend to blister but high strength steels tend to crack.

In addition, other forms of hydrogen charging (such as cathodic charging) result in cracking. Many of these charging mechanisms were described before the effects of hydrogen sulphide were recognized. Attempts to use familiar terms to describe hydrogen sulphide attack add to the confusion.

Industry now tends to classify the effects of hydrogen sulphide on steels as those that require the application of external stress, and those that do not (Ref. 76). The former is termed Sulphide Stress Cracking (SSC) and the latter, Hydrogen Induced Cracking (HIC).

4.1 Hydrogen Cracking Mechanism

Hydrogen in steels is generally recognized as coming from three main sources:

- (a) the corrosion reaction
$$\text{Fe} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 2\text{H} \text{ or } \text{H}_2,$$
- (b) electrolytical generation, or
- (c) the thermal dissociation of hydrogen or its compounds.

The effects of hydrogen on steel are classified generally as Cold, Hot, or Very Hot Hydrogen Effect.

4.1.1 Cold Hydrogen Effect

Cold Hydrogen Effect (below 190°C or 375°F) involves the penetration of steel by monatomic hydrogen.

Hydrogen is generated by the corrosive action of the sulphide solutions on the steel. Because this hydrogen is produced in the monatomic state it is able to penetrate the steel (Ref. 1), collecting at voids and fissures where it forms gas bubbles. Pressure builds in these bubbles and a blister or crack forms (see sections 7 and 8 for a detailed description).

This type of attack is experienced in the heavy water and sour gas industries and in some areas of refineries.

4.1.2 Hot Hydrogen Effect

Hot Hydrogen Effect (204°-482°C or 400°-900°F) involves hydrogen dissociating at the metal surface and penetrating the steel. This hydrogen combines with carbon in the steel to produce methane which exerts high aerostatic pressure resulting in cracking.

4.1.3 Very Hot Hydrogen Effect

Very Hot Hydrogen Effect (above 538°C or 1000°F) involves carbon migrating to the steel surface. There, it combines with hydrogen to form methane and leaves the steel.

Obviously, Hot and Very Hot Effects are not found in the heavy water industry. They may be encountered in sour gas wells, refineries and, to some extent, boilers.

5. THEORIES OF HYDROGEN DAMAGE

As with any failure mechanism numerous theories have been proposed to explain the effects of hydrogen on low alloy steels. They are summarized below.

5.1 Precipitation of Molecular Hydrogen in Microvoids (Zapffe and Sims, Ref. 196)

This theory suggests that monatomic or nascent hydrogen enters the steel in interstitial solid solution and is able to diffuse through the metal to naturally occurring voids such as grain boundary triple junctions, laminations, and non-metallic inclusions. Here it collects as molecular hydrogen, building in pressure until the yield strength of the material is surpassed and blisters form. Linking of blisters or fissures produces cracks.

5.2 Decohesion Theory (Troiano, Ref. 191)

This theory suggests that absorbed hydrogen can result in a reduction of the cohesive force of the metallic bonds of a material. If this reduction in the cohesive force is coupled with a high triaxial stress, an elastic separation of the lattice bonds can occur, producing a crack.

An incubation period, which is strongly dependent upon the level of hydrogen in the metal, is associated with this cracking mechanism. The length of the incubation period is influenced by the level of hydrogen in the steel and by the hydrogen diffusion rate. The diffusion rate may be stress related in that areas of high stress experience elevated diffusion rates.

For a crack to initiate, a critical level of hydrogen must be reached in an area of high triaxial stress. This area of high triaxial stress will occur just in front of an advancing crack tip. The implication is that crack propagation is a discontinuous process consisting of a series of crack initiations. When cracks form, they grow through the hydrogen-enriched area joining previous cracks. Further crack growth must await diffusion of hydrogen to the new region of high stress.

5.3 Theory of Brittle Fracture (Petch, Ref. 192)

This theory, based upon the Griffith theory of brittle fracture, suggests that hydrogen diffusing through a metal lattice will be adsorbed onto the internal surfaces of naturally occurring voids and fissures. The presence of the hydrogen lowers the surface energy necessary to create new crack surfaces, satisfying Griffith's criterion for crack extension. The crack tip provides a place to concentrate the stress necessary to form the new surfaces. As the crack spreads, the stress necessary to make it grow becomes less. When a critical crack size is reached, further propagation will occur catastrophically.

5.4 Hydrogen Wetting Theory (Nathan et al, Ref. 35)

This theory suggests that hydrogen migrating to non-metallic inclusions

preferentially wets the inclusions, destroying the bond between the inclusion and the matrix and resulting in a decohesion similar to that proposed in 5.2.

5.5 Dislocation Mobility Theory (Beachum, Ref. 193)

This theory suggests that concentrated hydrogen, dissolved in the lattice just ahead of the crack tip, will aid whatever deformation process the microstructure will allow. Intergranular, quasicleavage or microvoid coalescence fracture modes may occur, depending upon the microstructure, the crack-tip stress intensity, and the concentration of hydrogen. The theory suggests that instead of locking dislocations in place, hydrogen unlocks them, allowing the dislocations to multiply or to move at reduced stresses.

5.6 Summary

A combination of the Precipitation of Molecular Hydrogen (5.1) and the Decohesion (5.2) theories is probably most valid and may be used to explain most observations found in sour service failures (Ref. 52).

6. CORROSION OF ALLOYS BY HYDROGEN SULPHIDE

Hydrogen sulphide corrosion has received a good deal of attention in published literature, particularly concerning the effects on various alloys as manufacturers attempt to have their products listed in NACE MR-01-75 (Ref. 1). The corrosion is usually classified as to its effect upon the alloy and terms such as Sulphide Stress Cracking, Hydrogen Induced Cracking, Blistering, and Pitting are much in evidence. In addition, corrosion may also be classified easily as to alloy type. For example, while blistering is encountered in carbon and low alloy steels, it is not generally found in austenitic stainless steels and high nickel alloys. Consequently, corrosion by hydrogen sulphide has been subdivided, for the purposes of this report, by its effects upon carbon steels (6.1) and high alloy materials (6.2).

6.1 Carbon Steels

Corrosion by hydrogen sulphide on carbon steels involves corrosion under acidic or alkaline conditions. It has been classified in four pH ranges (Ref. 35).

- (1) At a pH below 4.5 acid conditions prevail and corrosion usually proceeds as $\text{H}_2\text{S} + \text{Fe} \rightleftharpoons \text{Fe}^{2+} + \text{S}^{2-} + 2\text{H}^+ + 2\text{e}^-$ (in general). The monatomic hydrogen is prevented from recombining as molecular hydrogen by the presence of the sulphide ions. This situation was termed poisoning in older papers (Ref. 37,56,74,61) but also is considered to be a bridging or ligament function, promoting hydrogen entry into the steel by making certain areas more susceptible to penetration (Ref. 35) (a wetting effect). As the pH decreases, corrosion increases in severity.
- (2) In the pH range of 4.5-6.0, corrosion rates tend to be lower due to the lower solution activity. However, corrosion does occur as per the equation above and hydrogen penetration of steel is still found as indicated by the BP Test (Ref. 165).
- (3) In the pH range of 6.0-8.0 corrosion may occur, due to the presence of breaks in scales or to the formation of discontinuous corrosion scales. Pitting may occur due to the formation of corrosion cells (Ref. 110).
- (4) Above pH 8.0, in the absence of cyanide ion, very low corrosion rates occur because of the formation of a protective scale. In the presence of cyanide ion, rapid corrosion and hydrogen blistering can occur (Ref. 33,37,38,40). This blistering and corrosion tends to disappear at a pH about 9.5 (Ref. 25).

6.1.1 Parameters Affecting Corrosion

The vast majority of corrosion reactions involves three main components - moisture, oxygen or an oxidizing substance, and an aggressive species capable of dissociating into an ionic state. Carbon steels do not corrode in dry hydrogen sulphide. Water is necessary for the corrosion reaction to occur (Ref. 56,74).

Oxygen also promotes the corrosion reaction (Ref. 33,141) and can result in rapid pitting even in the absence of other known pitting agents.

Moist hydrogen sulphide readily attacks carbon steel in either an acidic or alkaline reaction. It dissociates on the steel surface, permitting combination of iron and sulphide ions. The higher the hydrogen sulphide levels, the greater will be the rate of attack (Ref. 4,33) and resultant spread of damage.

6.1.2 General Corrosion

General corrosion results in overall attack of an alloy with metal loss over large areas. It is easily detected through weight loss coupons. This type of corrosion has been compared to the oxidation of carbon steels at high temperature (Ref. 83). Initially, the corrosion rate is high as fresh metal is exposed to the solution and a film rapidly forms on the surface. If the film is protective, the rate of scale formation decreases with time. Consequently, the rate of loss of the underlying metal also decreases.

General corrosion is the most manageable form of attack, as it permits prediction of service life, allowing planned shutdowns for replacement of components. Unfortunately, it rarely occurs in hydrogen sulphide service. Pitting is much more prevalent.

6.1.3 Pitting

Pitting in sour service is one of the most destructive forms of corrosion. It usually results in perforation of the material with only a small weight loss of the entire component (Ref. 85). It is difficult to detect because of the presence of deposits and because of the relatively small size of the pits. It is autocatalytic in nature and the rate of penetration accelerates with time. Iron sulphides depositing on the surface may promote the formation of local anodes and the presence of chlorides increases the penetrating power (Ref. 18). Through-wall penetration can occur in a few weeks.

Deposits, damming the pipelines and, therefore, keeping moisture in the system, can lead to pitting (Ref. 66). Pits form generally in the bottom quadrant of components and are usually isolated (Ref. 83). They display an "Oyster Shell" pattern, characteristic of sulphide attack (Photograph 1), and may be quite large although overall metal loss is small.

Pits also contribute to sudden brittle fracture as they are often the initiation sites for Sulphide Stress Cracking (Ref. 29).

6.1.4 Protective Scales

Pitting, general corrosion and, especially, Sulphide Stress Cracking and Hydrogen Induced Cracking, may be reduced and even eliminated by the formation of a protective sulphide layer on the steel (Ref. 10,174). This sulphide layer may be produced intentionally through preconditioning of the steel prior to service, (Ref. 10,174) or it may form during normal operations (Ref. 110). In

any case, certain sulphides such as pyrite and, to a lesser extent, troilite (Ref. 174) have been found to be protective, whereas unstable mackinawite tends to be non-protective or, if it is porous, may even accelerate corrosion. This is particularly true in the presence of sodium chloride.

Certain alloying elements added to the carbon steel promote the formation of films and/or stable scales, thereby reducing the corrosive attack on the steel. Films and scales also reduce the amount of hydrogen penetration in steels. Copper has been found effective, provided the pH of solutions is above 5.0 (Ref. 2,41,133). In addition, copper in combination with cobalt has been found effective in lower pH solutions as well (pH 3 - 3.5) (Ref. 129). Manganese and nickel also have been found effective under certain conditions (Ref. 70, 168). Their effects upon the alloy are so controversial that they are outlined in more detail elsewhere (Section 7 and 8).

The effects of many of the alloying elements are considered to be dependent upon an affinity for hydrogen. This affinity either raises the level required for cracking the alloy or, prevents the collection of hydrogen at non-metallic inclusions by somehow forming a coating on them (Ref. 129).

6.1.5 Erosion

In order to prevent excessive attack on carbon steel, formation of a protective scale may be encouraged. Velocities must be restricted to prevent removal of the scale due to erosion. If the scale is removed, the underlying steel can experience corrosion rates approaching 25mm per year (Ref. 83,174). Considerable hydrogen is generated by the corrosion and it can penetrate the steel, producing blisters and Sulphide Stress Cracking (Ref. 83,85,141, 142).

Velocities are generally restricted to 2.1 metres/second in liquid phases and 18 metres/second in gaseous environments (Ref. 83,85), although there are indications that erosion can occur with gas velocities over 6 metres/second (Ref. 157). In any case, removal of the sulphide scales, whether it be by erosion or chemical attack, must be prevented.

Acids and alkaline solutions will remove these protective scales (Ref. 145). The normal passivating or sweetening methods used prior to opening equipment do not harm the scales. However, re-exposure of passivated scales results in an initial high corrosion rate which quickly reduces to normal rates. Steaming and moist air appear to be more damaging to the scales than neutralization (Ref. 101).

6.1.6 Sulphide Stress Cracking and Hydrogen Induced Cracking

Sulphide Stress Cracking and Hydrogen Induced Cracking are the most commonly studied effects of hydrogen sulphide on carbon and low alloy steels. A sudden brittle fracture may occur in a pressure envelope or an easily visible hydrogen blister may form on the wall.

It is generally accepted that SSC and HIC are associated with hydrogen in the metal (Ref. 74,154). Gas in blisters has been analyzed and found to be largely hydrogen with minor amounts of methane, carbon monoxide, carbon dioxide and nitrogen (Ref. 74, 124,138). Also, pressures in blisters have been relatively high, of the order of 68.9 - 186.2 MPa (1000-2700 psi) in a system operating with a maximum internal pressure of 18.62 MPa (270 psi).

Damage that results in blistering, fissuring, and Step-Wise Cracking in carbon and low alloy steels is referred to as Hydrogen Induced Cracking (Ref. 29,79,154). It can occur in materials without the application of external stress (Ref. 76). It has been also identified as a component of some Sulphide Stress Cracking failures (Ref. 80). In these cases Hydrogen Induced Cracking may have initiated at non-metallic inclusions. Stresses created by hydrogen blisters may reach levels high enough to promote Sulphide Stress Cracks. These cracks tend to propagate in the through metal direction.

Hydrogen Induced Cracking occurs when monatomic hydrogen, produced by the corrosion of the steel by the sulphide solution, penetrates and diffuses through the steel until it is trapped at a naturally occurring barrier in the steel. Elongated manganese sulphides, alumina particles (Ref. 26,75) complex carbonitrides, and glassy silicates (Ref. 26,75) have all been identified as initiation sites for Hydrogen Induced Cracking initiation. (Photographs 2,3,4,5)

Hydrogen Induced Cracking forms parallel to the rolling direction of the steel (Ref. 76) and is strongly dependent upon the segregation of manganese and phosphorus in the ingot (Ref. 137). Consequently, cracking is often found in pearlite, bainite, or untempered martensite bands (Ref. 133). Lowering the sulphur content to less than 0.001% results in substantial improvement in crack resistance due to the reduction in manganese sulphide inclusions (Ref. 2,75, 131). As well, additions of calcium and, to a lesser extent, of rare earth metals prevent the sulphide inclusions from becoming elongated, reducing susceptibility to HIC (Ref. 75,107,112, 142).

Steels containing large quantities of non-metallic inclusions, primarily manganese sulphides, have cracked and blistered in non-sour acid media. Corrosion of the sulphide inclusions by the acid produces the hydrogen sulphide necessary for the attack (Ref. 63). In addition, differences in thermal expansion between the non-metallic inclusions and the metal matrix may promote the opening of cracks (Ref. 135), particularly if corrosion or hydrogen charging has occurred.

Blistering and/or cracking in carbon steels is linked to both a critical threshold strength (Ref. 17) and to a critical level of hydrogen in the steel (Ref. 41,45,115). If blistering or cracking is to occur, the critical threshold strength, frequently approaching the yield strength of the material, must be exceeded by the hydrogen pressure building at non-metallic inclusions. This threshold strength will not be reached if there is insufficient hydrogen in the steel to develop the required pressure.

Once hydrogen blisters have formed, they may link to produce a Step-Wise Cracking pattern. As blisters approach one another, the ligament of solid metal between them becomes smaller (Photographs 6,7). Eventually the stresses in the adjacent blisters become so high that the ultimate tensile strength of the small metal ligament between them is exceeded and tearing occurs. This linking, in the absence of external stress, takes place between blisters in different planes, producing the Step-Wise appearance (Ref. 154). With external stress, blisters may still link, by tearing the metal between them, but these blisters will be in a stacked array, producing a crack perpendicular to the stress direction.

Hydrogen Induced Cracking has not been identified in welds (Ref. 6,42). This may be due to the cast structure which displays greater resistance to failure than a similar wrought product (Ref. 9) or it may be due to heat treatments and the absence of elongated non-metallic inclusions, but certainly one would expect that slag inclusions would be ideal sites for the collection of diffusing hydrogen.

Sulphide Stress Cracking, on the other hand, frequently occurs associated with welds, either in the heat affected zone or in the weld metal itself (Ref. 7,30, 164,167). It is defined as brittle fracture occurring at right angles to the direction of stress (Ref. 76,154). SSC generally occurs in materials with hardness values over Rc 22 (Ref. 163) although lower hardness levels are set for safe operation of welds in refineries. (Ref. 153,167)

Failure is usually the result of a single straight crack with limited branching (Ref. 109). Tensile strength must be considered as high strength materials tend to show considerable branching when subject to SSC (Ref. 4). The crack frequently initiates from a corrosion pit (Ref. 147) where stress raisers would occur. (Photographs 8,9)

Alloying elements such as manganese, nickel, and carbon that can result in hard structures promote the cracking. Cracking frequently occurs along prior austenite grain boundaries and in untempered bainite and martensite (Ref. 107,109, 167). Quenched and tempered structures appear to be the most resistant to this form of attack (Ref. 130,94,116).

Sulphide Stress Cracking is encouraged by low pH (Ref. 3,25), cold working (Ref. 25), high tensile or residual stresses, and relatively low temperatures - in the neighbourhood of 5-50°C (Ref. 19,28).

6.1.7 Hydrogen Charging

Hydrogen generated electrolytically at cathode areas may also penetrate the steel, producing blisters and cracks in susceptible materials. Experiments in both operating environments and laboratories suggest that hydrogen generated by the galvanic coupling of carbon steel to more noble materials can result in blistering in materials that would perform satisfactorily in an uncoupled state (Ref. 49). As well, breaks in coatings on cathodically protected pipelines have produced conditions of hydrogen charging which lead to blistering.

6.1.8 Heat Treatment

In order to combat SSC, the residual stresses in carbon and low alloy steels are lowered by heat treatment. This procedure is generally a stress relief and attempts are made to produce structures resistant to brittle fracture. Charpy Impact tests are often employed to measure the alloy's response. It is felt that tough ductile steels are less likely to suffer from the brittle fracture associated with SSC. If cracks or blisters do form, it is hoped that propagation in a brittle manner will not occur.

Heat treatment of the steels will be successful only if hard spots (Ref. 30) in weld heat affected zones can be softened. Shot peening (compressing a surface by striking it with metal shot), advocated in place of thermal treatments, and perhaps beneficial in mild environments, cannot eliminate hard structures which are subject to diffusing hydrogen. In addition, excessive surface compression can result in crack promotion due to severe cold working.

Normalized and tempered (Ref. 153) or quenched and tempered structures (Ref. 94) appear to be the most resistant to cracking, although care must be exercised in choosing the correct heat treatment.

6.2 High Alloys including Austenitic Stainless Steels

Austenitic stainless steels and other high alloys generally rely upon a thin oxide layer to impart corrosion resistance. If this layer is penetrated, more severe corrosion can occur.

6.2.1 Pitting

In sulphide solutions, pitting is encountered most frequently in the lower grade austenitic alloys, such as Type 304 (Ref. 83,95). Randomly oriented, pitting generally occurs due to the presence of chlorides (Ref. 83,85,95). Moisture is necessary for this form of attack. (Photograph 10)

As in carbon steels, pitting in austenitic alloys is autocatalytic in nature with the rate of penetration increasing with time. Detection of this pitting can be difficult as perforation may occur without significant weight loss in the component (Ref. 83,85). Besides perforation, cracking due to stress concentration may initiate from corrosion pits.

The addition of such elements as molybdenum greatly enhances an alloy's pitting resistance by forming very stable films.

6.2.2 Stress Corrosion Cracking

Stress Corrosion Cracking, as the name implies, involves cracking of stressed components in a corrosive environment. Perhaps the best example of this form of attack is the action of chloride-containing solutions on stressed austenitic stainless steels. Transgranular, branching cracks develop after an incubation period. The length of this stage is affected by several factors. The solution then seeps through these cracks and the component fails.

Hydrogen sulphide environments frequently contain high levels of chlorides. This is particularly true of "downhole" conditions where gas and oil wells often encounter salt domes and other chloride-containing materials (Ref. 23). Consequently, laboratory experiments investigating the resistance of high alloy materials to sulphide environments include stress corrosion cracking tests.

Austenitic stainless steels will suffer transgranular stress corrosion cracking in hydrogen sulphide solutions when chlorides are present (Ref. 95, 102). The presence of oxygen is necessary to crack most alloys although Types 304 and 347 stainless steels, along with the martensitic and ferritic grades, will crack without oxygen (Ref. 95, 102). (Photograph 11)

Duplex alloys (an austenite-ferrite mix) have shown a mixed reaction to solutions containing hydrogen sulphide. In some instances, cracking resistance has been excellent and in others, it has been poor. Cracking has been observed between the austenite-ferrite grains (Ref. 106) with general transgranular cracking of the alloy. This response may be attributed to low nickel contents (Ref. 93) or to cold working (Ref. 23), or, to the fact that the alloy was not appropriate for particular test environments.

Temperature and hydrogen sulphide concentration must be balanced for duplex alloys to perform well. The alloys show good cracking resistance at low temperatures with low hydrogen sulphide levels (Ref. 31). Raising the temperature with the low hydrogen sulphide levels results in increased cracking. With high hydrogen sulphide levels, raising the temperatures decreases the cracking. One must be extremely cautious in the use of these alloys ensuring that corrosion testing is performed in a service environment.

Higher nickel alloys generally show good resistance to cracking in sulphide solutions as long as they have not been severely cold worked (Ref. 49). However, many of these alloys, particularly those that undergo precipitation hardening, require special heat treatments to make them resistant to cracking. While there is no doubt that many of these special alloys can be used successfully in sour environments, complicated and multi-step heat treatments can be both costly and potentially dangerous. Each stage in a multi-step process has potential for error, which could create structures that will fail in service. In addition, the more complicated the heat treating, the more difficult will be field repair in the event of failure.

Lately, numerous materials have been submitted to NACE for inclusion in NACE MR-01-75. Many of these involve complicated heat treatments; double overaging, aging and tempering, and mill annealing with double overaging, to name but a few. Errors in specifying or accomplishing the proper treatments can lead to failure. Consequently, one would be advised to use materials with relatively simple heat treatments.

6.2.3 Intergranular Corrosion

Austenitic stainless steels and other high nickel alloys can experience sensitization during heat treatment or welding. Sensitization involves precipitation of

chromium carbides at grain boundaries, lowering the corrosion resistance of the adjacent material. Intergranular corrosion occurs in hydrogen sulphide environments due to the formation of sulphur-oxy-acids in the presence of oxygen (Photograph 12). Stabilized grades or low carbon materials are used in the hope of avoiding this sensitization. However, these materials may be sensitized by multiple heat cycles or long times at high temperatures.

Solution annealing is employed to prevent this sensitization.

6.2.4 Deposit Corrosion

Austenitic stainless steels, particularly Type 304, are prone to a deposition attack in hydrogen sulphide solutions (Ref. 83,85). Differential aeration cells may be created on the material surface, leading to corrosion around the edges and underneath the deposit. Corrosion rings or "flow marks" are often found, indicating successive limits of the deposit (Photographs 13,14).

6.3 Summary

Corrosion by sour environments is classified as to its effects upon carbon steels and high alloy materials as follows:

6.3.1 Carbon Steels

Corrosion of carbon steels in sour environments occurs in the presence of water. Oxygen acts as a promoter, particularly under acidic conditions, increasing the rate of attack. The corrosion can be classified in four pH ranges:

- (1) below 4.5 where acid conditions prevail with active corrosion,
- (2) in the range of 4.5-6.0 where corrosion rates are somewhat lower,
- (3) in the range 6.0-8.0 where corrosion occurs due to breaks in scale,
- (4) above pH 8.0 where very low corrosion rates occur but, if cyanide ions are present, rapid attack takes place.

Corrosion ceases above pH 9.5.

Corrosion is also categorized by the type of attack.

- (1) General corrosion results in an overall attack with metal loss over large areas.
- (2) Pitting corrosion results in perforation of the component with little overall metal loss. The pits are generally randomly oriented, below the liquid's surface.
- (3) Erosion/Corrosion is a term used to describe removal of protective scales by process stream velocities, exposing the underlying steel to high corrosion rates. Corrosion rates can approach 25 mm per year under these conditions.

- (4) Sulphide Stress Cracking, a brittle fracture of the metal occurring at right angles to an applied stress, is characterized usually by a single straight crack. It occurs in association with welds, either in the weld metal itself or in the heat affected zone.
- (5) Hydrogen Induced Cracking occurs when monatomic hydrogen, produced at the steel surface by corrosion, migrates to and collects at non-metallic inclusions, creating blisters. These blisters may link to form cracks. External stress is not necessary to form cracks.

Corrosion and cracking of the carbon steels may be reduced by the presence of a stable sulphide scale on the steel surface. However, low pH coupled with high hydrogen sulphide concentrations can result in dissolution of the scale.

6.3.2 High Alloy Steels

High alloy steels, such as austenitic stainless steels, are basically resistant to attack by sour environments if chlorides are not present. Sulphide Stress Cracking can occur in severely cold-worked material. Hydrogen Induced Cracking has not been identified in the high alloys.

Corrosion is again categorized as to the type of attack.

- (1) Pitting is encountered in the lower grade alloys such as Type 304, particularly in the presence of chlorides.
- (2) Stress cracking occurs typically as transgranular cracking with some branching tendencies. The presence of chlorides is generally necessary for the cracking to occur. Lower grade alloys such as Type 304, or martensitic and ferritic type alloys, will crack in the absence of oxygen. Oxygen is necessary to crack the higher grade alloys.
- (3) Intergranular Corrosion occurs in alloys that have been sensitized through heat treatment. Cracking follows an intergranular path and can occur in the absence of external stresses.

6.3.3 Complex Alloys

Numerous new alloys have been proposed for sour service. These alloys generally require complex, multi-step heat treatments to be crack resistant. Each step in the process provides potential for error. In addition, complicated heat treatments make field repairs more difficult. Consequently, alloys with the simplest heat treatments should be employed.

7. SULPHIDE STRESS CRACKING

Sulphide Stress Cracking is characterized by an initial, single, straight transgranular crack (Ref. 109) that develops under the application of a tensile stress, either applied or residual. It occurs at right angles to the direction of the applied stress. Frequently initiating at corrosion pits, it propagates, branches and stops (Ref. 147). Branching tends to be related to the tensile strength of the steel; low strength steels show little branching while there is considerable in high strength steels.

Another feature of SSC is that it occurs frequently in association with welds (Ref. 7,30,164). The cracks may be in the weld metal itself (Ref. 164,167) or in the heat affected zones (HAZ), particularly at hard spots (Ref. 30). These hard spots are not affected by standard heat treating practice (Ref. 117,150).

Certain semi-automatic or automatic welding processes severely reduce SSC resistance. In submerged arc welding, an injudicious choice of welding procedure and flux can produce high concentrations of manganese and silicon in the weld deposit (Ref. 167). High concentrations of these elements result in hard microstructures which tend to crack. For this reason, preliminary testing of welding procedures and consumables seems advisable.

As well, it has been determined that some welds made with the Gas Tungsten Arc Process and using the filler metals E70S-2 or E70S-6 were more subject to preferential corrosion in sour environments than were Shielded Metal Arc welds (Ref. 81). Shielded Metal Arc root passes, or backfill, even in combination with susceptible Submerged Arc, did not crack in service, probably because high concentrations of manganese and silicon are unlikely in the Shielded Metal Arc Process.

Normally, SSC occurs in carbon steels or low alloys with tensile strengths greater than 772.2 MPa (112,000 psi) (Ref. 163). In very severe environments, this strength level is too liberal and 551.6 MPa (80,000 psi) is suggested as a more reasonable and safe level (Ref. 3). A relatively simple test (hardness) may be used to determine the strength level of a material.

Hardness tests usually employ an indentation technique in which a small impression is made in the metal. Resistance to the indentation is directly related to the compressive strength of the material. For most carbon and low alloy steels, there is a close relationship between compressive strength and tensile strength. Therefore, indentation hardness values can be used to estimate tensile strength with reasonable accuracy (± 34.47 MPa, 5,000 psi).

Rc 22 and BHN 235 are most used as the hardness figures approximating the safe limits for alloys in sour service. These values have been established through field experience and are those contained in most sour service material standards. In refineries, cracking of welds has been experienced at hardness levels below BHN 235 so BHN 200 is often used as the maximum safe limit if high residual stresses can exist.

The response of parent materials suggests that while the Rc 22 level is a reasonable guideline, it should not be considered absolute. Both field and laboratory tests have indicated that cracking did not occur in material with hardnesses of Rc 24-26 (Ref. 160). Alloys with hardnesses up to Rc 29 (Ref. 148) may be used successfully, depending on alloying additions and on the heat treatment. In other cases, cracking occurred in sour environments at hardnesses well below Rc 22 (Ref. 164). Probably the microstructure, not the alloy composition, governs a material's response to sulphide solutions (Ref. 150).

Sulphide Stress Cracking is further complicated by the fact that Hydrogen Induced Cracking (discussed in Section 8) often accompanies it. In addition, Sulphide Stress Cracking may occur in association with blisters (Ref. 76). The main SSC crack at failure has been found to connect pre-existing planar-oriented cracks and a subsidiary crack (Ref. 43).

Resistance to Hydrogen Induced Cracking does not necessarily mean resistance to Sulphide Stress Cracking (Ref. 44,107). In fact, it has been suggested that decreased resistance to HIC can be correlated with increased resistance to SSC (Ref. 88). However, it is generally said that a steel that resists blistering also has a microstructure that may be resistant to cracking due to the controlled inclusion shapes or to the reduction of harmful alloying elements such as sulphur (Ref. 75).

7.1 Microstructure

Although hardness is used as the criterion for determining an alloy's resistance to cracking in sour environments, microstructure is an aspect that should be given as much attention (Ref. 116,150). For instance, fine grained acicular ferrite (Ref. 170) has greater resistance to cracking than does a martensitic structure of the same hardness. Spheroidized carbides, followed by tempered structures, present the greatest resistance to cracking (Ref. 87). In high strength, low alloy materials, quenched and tempered martensitic structures are the most resistant (Ref. 94).

Sulphide Stress Cracking tends to occur in hardened zones, particularly those involving untempered martensite or upper bainite (Ref. 107,109). Segregation bands, consistent with these low transformation temperature structures, are also areas in which high concentrations of manganese and phosphorus are found (Ref. 75,42,134). Consequently, they are prime sites for cracking. In addition, Sulphide Stress Cracks propagate discontinuously along former austenite grain boundaries (Ref. 52). Heat treatments, therefore, must involve, first, temperatures high enough to affect the structure and, second, rapid cooling.

Sulphide Stress Cracking resistance will be increased by heat treatments that refine the austenite grain size. This is achieved by raising the treatment temperature. Care must be exercised in controlling tempering temperatures as a fully quenched and tempered martensitic structure must be obtained. Tempering above the AC1 point (the austenite/ferrite transformation temperature) followed by water quenching, can severely degrade the material (Ref. 87).

7.2 Alloying Elements

Alloying elements must be selected carefully to prevent weak structures or excessive hard zones.

Manganese has been found either to increase the susceptibility to cracking (Ref. 50,72) or to reduce it slightly (Ref. 70,169). The results are highly dependent on the pH of the test solution as manganese can form a protective scale on steel with a pH above five. This scale reduces the corrosion rate and, therefore, the hydrogen available for charging. The possibility of cracking is also reduced (Ref. 173).

On the other hand, manganese in an alloy can promote hardening, producing structures that are prone to cracking (Ref. 167). Consequently, increasing the manganese content of the alloy must be weighed carefully against the prospects of producing hardened zones of untempered martensite and banded structures (Ref. 78).

Molybdenum, particularly in the absence of chromium, has a pronounced beneficial effect on the SSC resistance of low carbon alloys (Ref. 61,70). Molybdenum is added to an alloy and to welding consummables to improve the Charpy Impact properties of a steel. However, if copper is present in the alloy, molybdenum additions will increase the corrosion rate greatly (Ref. 171).

Chromium additions appear to have a mixed effect on low alloy steels with respect to SSC. In solutions with a pH 5.0 or higher, chromium additions reduce hydrogen entry into the steel, probably through formation of a protective scale (Ref. 171). As the pH decreases, the beneficial effect of chromium decreases. The positive effect disappears at a pH around 4.0. In solutions with a pH lower than 4.0, chromium additions produce an increase in the amount of diffusible hydrogen in the steel (Ref. 70,72).

Niobium and titanium significantly raise the threshold stress for cracking (Ref. 75). They are added frequently to increase the toughness of an alloy. The effect may be due entirely to the titanium as niobium appears to have no influence (Ref. 70). The additions may prevent SSC by altering the nature of the carbide/matrix interface.

The carbon content of steels destined for sour service can have a great influence on SSC resistance. Increasing the carbon content generally increases the SSC cracking susceptibility (Ref. 155). This is due to the influence that carbon has on the microstructure and on the hardness.

As the carbon content increases, there is a greater potential for retaining low transformation temperature structures upon cooling from heat treating conditions. Consequently, tempering is extremely critical.

The influence of carbon is usually determined through use of an empirical relationship termed the carbon equivalent (CE). This seeks to establish the hardenability characteristics of a steel based upon its chemistry. Field tests suggest that materials with a CE less than 0.35 may be highly resistant to SSC provided the effects of all other alloying elements are considered (Ref. 148).

Nickel additions to alloys for sour service are restricted to a maximum of 1% by NACE MR-01-75 and other standards. This level is based on both field and

laboratory experience in which cracks occurred in alloys with a higher nickel content (Ref. 70,152,160). The cracking was associated frequently with welds but also occurred in unwelded parent metal.

Nickel additions to alloys are highly desirable to promote weldability and toughness properties. Many studies have been undertaken in attempts to have the nickel restrictions removed for alloys and welding consumables. A number of these studies conclude that nickel is not detrimental to SSC resistance (Ref. 57,139). In fact, they suggest that nickel has a beneficial effect on SSC resistance.

A literature survey on the subject concluded that there was no scientific proof either for or against the use of nickel in alloys to resist Sulphide Stress Cracking (Ref. 71). However, examination of articles, both pro and con, indicates that the influence of other alloying elements has been largely ignored. Beneficial and/or detrimental effects of these other alloying elements may be responsible for some of the test results. Considerable work is necessary to establish clearly the influence of nickel before anyone should consider removing the 1% level imposed by the standards.

7.3 Crack Morphology

Sulphide Stress Cracking includes crack initiation and crack propagation phases. Cracking occurs only after an incubation period but this period may be very short. The crack initiation may be governed by the corrosivity of the environment, the presence of protective scales, and the alloy composition. Crack propagation is a function of the corrosive environment and the stress. Therefore, cracks may occur and propagate in an alloy in one service environment and yet be totally absent under similar conditions in another, slightly less corrosive environment.

Cracks that form under sulphide conditions generally propagate to failure in a brittle manner. Frequently, the final failure is a ductile overload fracture when the cross-section has been reduced enough to allow plastic deformation under the applied load (Ref. 140). Fracture surfaces, therefore, tend to show both a brittle and, to a lesser extent, a ductile mode.

Sulphide Stress Cracking may be controlled by using alloys heat treated for specific environmental conditions. For example, quenched and tempered structures are recommended but only if the structure has been fully transformed (Ref. 144). pH must also be considered as the lower the pH, the higher the rate of attack and, hence, the more hydrogen that is available to penetrate the steel (Ref. 149). Hardness levels of Rc 22 might not be adequate to prevent cracking as it is the microstructure that is important (Ref. 116,140). Increasing the temperature also results in lowering the SSC susceptibility.

7.4 Other Environmental Variables

Besides pH and H₂S concentration, other environmental factors affect the SSC properties of an alloy.

Sulphide Stress Cracking is strongly temperature-dependent. Most cracking occurs in the 5-50°C range (Ref. 19,28). As temperatures rise above 50°C the cracking susceptibility of the steel decreases.

Cracking tendencies can be retarded by the application of an electrical potential, suggesting that an electro-chemical reaction is responsible for the cracking phenomenon. Application of an inappropriate potential can result in excessive hydrogen charging and, as a result, increased cracking.

Inhibition is another technique to influence environmental effects on SSC. Employed in the sour gas and refining industries, the inhibitors, usually proprietary compounds, are injected into process streams and drilling muds to form protective films on alloys. These films reduce the amount of corrosion and, also, the hydrogen charging of the steels.

7.5 Summary

Sulphide Stress Cracking is a complex problem because it involves variables such as pH (Ref. 19,35,42,65,114), applied electrical potential (Ref. 6,19), applied stress (Ref. 25), temperature (Ref. 19,153), inhibition (Ref. 5, 74,157), hydrogen sulphide concentration (Ref. 4,30,59) and metallurgical factors (Ref. 24,118). In addition, operating conditions that change suddenly can create environments conducive to failure.

7.5.1 Cracking Characteristics

Sulphide Stress Cracking involves brittle fracture of carbon and low alloy steels due to a hydrogen cracking mechanism. Cracking occurs under the application of an external stress, either applied or residual. The cracks propagate at right angles to the applied stress.

An SSC crack displays the following characteristics:

- (1) It is usually a single straight, transgranular crack with limited branching. The branching is associated with the tensile strength of the material: the higher the tensile strength, the more extensive the branching.
- (2) The crack frequently occurs in association with welds, either in the weld metal or in the heat affected zone.
- (3) The crack frequently is associated with hydrogen blisters in low strength steels. The high aerostatic pressure in the blisters produces the stress necessary for cracking.

7.5.2 Metallurgical Factors Affecting Cracking

There are a number of variables that affect the cracking resistance of the alloy.

- (1) Microstructure - Cracking occurs in the low transformation structures such as martensite and bainite. Segregation of alloying elements such as manganese and phosphorus during solidification promotes hardening tendencies.
- (2) Heat Treatment - Heat treatments must modify or temper the low transformation structures. Most commercial heat treatments are inadequate if high segregation has occurred. Tempered martensite appears to produce the most resistance to cracking in susceptible materials.
- (3) Hardness - The hardness versus tensile strength relationship is employed to select steels resistant to cracking. Rc 22 is considered the maximum safe hardness limit, although failure in materials with lower values has been encountered, particularly in welds. The failure is related to the severity of the environment and to high stresses. However, alloys with hardnesses above Rc 22 can be used successfully in sour environments, provided the structure has been tempered properly. It is the structure, not the hardness, that will govern the alloy's cracking resistance.
- (4) Alloying Elements - A number of alloying elements may be added to the material in attempts to increase cracking resistance. Molybdenum, manganese and chromium are all considered beneficial. However, manganese can increase hardening tendencies, promoting cracking. Nickel additions should be kept to less than 1% to prevent hardening and cracking. Although a number of recent studies have suggested that there is no basis for the nickel restriction, field experience and numerous test results suggest further work is needed before changes are made.

Table 7.1: Sulphide Stress Corrosion Cracking Failures

Description	Material	Heat Treatment	Hardness in Fracture Area (Rc)	Phase	H ₂ S % Content	Environment		Date
						Location		
LOW ALLOY STEELS								
Casing	API Grade N-80	---*	---	Condensate and Gas		Ginger, Texas		1951
Tubing	9 NI Tubing	N&T	---	Gas	10	Pincer Creek, Canada		1951
Tubing	9 NI Tubing	---	---	Gas	7.5	McKamie-Patton field, Arkansas		1951
Tubing	9 Ni Tubing	---	---	Gas	7.5	McKamie-Patton field, Arkansas		1951
Casing	API Grade N-80	---	---	Gas	3.5	Jumping Pound, Canada		1954
Tubing, Coupling	API Grade N-80	---	51	Gas	3.5	Jumping Pound, Canada		1954
Casing	API Grade N-80	---	---	Gas	>10	Okotoks, Canada		1958
Casing Collars	API Grade N-80	---	25	Gas	trace	Paloma field, Calif.		1956
Tubing, Upset	API Grade J-55	not normalized after upsetting	25-39	Gas	>10	Okotoks, Canada		1958
Tubing	API Grade C-75	N&T	26-30 (Manganese-rich bands)	Gas	70	Panther River, Canada		1964
Casing Collars	SOC95	N&T	>25	Gas		Panther River, Canada		1966
Tubing	API Grade C-75	N&T	28-42	Sour Crude		South Texas		1966
Tubing	API Grade C-75	N&T	(Cold Rotary straightened) 22-24 (micro-hardness 41 in Tong Marks)	Sour Crude		Goodwater field, Miss.		1970
Compressor Valve Springs	AISI 6150 Free machining steel (S ₇₀ .28% - P ₇₀ .08)	---	38	Gas	>10	Pachuta Creek, Miss.		1970
Valve Manifold	---	---	---	BHN-156		Wildcat Hills, Canada		1962
Retainer Rings, Wellhead Tubing	---	---	51	---		Canada		1962
Hanger	AISI 4140	---	41-43	Low Temp.		Canada		1961
Blowout Preventor, Capstan Screws	AISI 4140	---	30-40	Condensate & Gas	>10	Waterton, Canada		1961
Bolts, Sphere-Here	AISI 4140	O&T						.../2

Table 7.1: Sulphide Stress Corrosion Cracking Failures (Cont'd)

Description	Material	Heat Treatment	Hardness in Fracture Area (Rc)	Environment		Date	
				Phase	H2S % Content		Location
LOW ALLOY STEELS							
(Cont'd)							
Christmas Tree Caps	AISI 4340	Cast & normalized	27-30	Condensate & Gas	>10	Waterton, Canada	1962
Christmas Tree Caps	AISI 4340	Cast & normalized	27-30	Condensate & Gas	>10	Waterton, Canada	1962
Dr Tubing Hange	---	---	26-29	Condensate & Gas	>10	Waterton, Canada	1962
Tool Joint Pin	Grade E	---	34-35	Gas & Mud	---	Waterton, Canada	1963
Drill Pipe	Grade E AISI 4135	---	---	Gas	70	Panther River, Canada	1968
Tool Joints	S-135	---	36-37	Gas & Mud	>10	Jonathan Area, Miss.	1970
Drill Pipe	HT-80(0.8NI)	---	23-25.5	Sour Water	Trace	---	---
Sucker Rods	HT-80(0.8NI)	---	---	LPG	Trace	Japan	---
LPG Tanks, Weld Area	TT-70.(0.8NI)	---	---	LPG	Trace	Japan	---
LPG Tanks, Weld Area	HT-60(0.03)	---	---	LPG	Trace	Japan	---
LPG Tanks, Weld Area	Low Alloy	Q&T(114,000 psi yield)	---	---	---	Hydrotreating Service (Gulf)	1968
Compressor Impeller	Ledloy A(Free-machining steel)	Cold Finished	BN-174	Condensate & Gas	10	Waterton, Canada	1963
Valve Bonnet							

After Treseder (Reference 153)

(---* no information given in original)

8. HYDROGEN INDUCED CRACKING (HIC)

Hydrogen Induced Cracking of steels is as complex as Sulphide Stress Cracking and many of the same variables are involved. Whereas Sulphide Stress Cracking occurs only under the application of an external stress and the crack propagates at right angles to this stress (Ref. 76,154), Hydrogen Induced Cracking can occur in the absence, or presence, of an external stress. HIC normally propagates parallel to the rolling direction of the steel (Ref. 76,154, 161).

Hydrogen Induced Cracking occurs when monatomic hydrogen generated at the steel surface by corrosion, penetrates the steel. The hydrogen is able to diffuse through the steel until it is trapped at naturally occurring voids such as non-metallic inclusions and laminations (Ref. 35,76,154). The hydrogen collects at these voids as molecular hydrogen. As hydrogen continues to diffuse to these voids, gas pressure builds until the yield strength of the alloy is reached and a blister forms (Ref. 29). A schematic illustration may be found in Figure 8.1.

The corrosion is represented by the simplified equation, $\text{H}_2\text{S} + \text{Fe} \rightleftharpoons \text{Fe}^{++} + 2\text{H}^+ + \text{S}^{2-} + 2\text{e}^-$. This chemical reaction would cease if the monatomic hydrogen could recombine to form molecular hydrogen at the steel's surface. The molecular hydrogen would coat the steel and prevent further corrosion. The presence of some sulphides, in particular hydrogen sulphide, prevents this recombination in what is termed a poisoning action (Ref. 37,56,74,161). Under alkaline conditions in a refinery atmosphere, cyanides have a similar poisoning effect (Ref. 33,37,38).

The orientation and shape of the non-metallic inclusions has a profound effect upon HIC resistance. If the inclusions are elongated by rolling or extrusion operations, the long dimensions will be at right angles to the diffusion path. This exposes more surface area to capture hydrogen than would be the case in a rounded inclusion of the same volume. In addition, stresses required to create a crack in a long, thin inclusion would be considerably lower than in the idealized rounded configuration (based upon simple fracture mechanics). Obviously, metal rolling practices that produce elongated sulphides will result in increased susceptibility to HIC (Ref. 137,142).

Hence, both steel-making practice and processing can affect a material's performance. Yet steels continue to be used in hydrogen sulphide service without failure even though diffusing hydrogen has been detected. There must be factors, other than the mere presence of hydrogen, that cause cracking.

The most obvious aspect to be considered is the amount of hydrogen in the steel. HIC is usually related to the diffusion of hydrogen in the steel (Ref. 55,142, 154). Cracking will occur if the amount of hydrogen diffusing in the steel reaches a critical level designated as C_0 (Ref. 115,191) and if this level is higher than that required to produce a crack (see Figure 8.2). Such hydrogen levels are often found in moist sour gas environments. The levels tend to be lower under liquid phase corrosion even if the rate of attack is high (Ref. 142) (see Table 8.1). Some indication of the critical level for HIC may be found in

that cracking occurred in Heavy Water Plant applications with a hydrogen flux of 6^μg/g but not at lower levels of 3.5^μg/g (Ref. 142,143).

The hydrogen flux to cause cracking is also affected by the charging mechanism. In many laboratory tests, samples, immersed in fluid, are subject to all-sided charging but plant piping and vessels experience one-sided charging. Therefore, a hydrogen gradient will exist as hydrogen is removed on the outside of the equipment. Measurement, with suitable probes, of the hydrogen passing through the wall, may determine the cracking and blistering resistance of a component (Ref. 11,36,92,162). Still, it must be remembered that hydrogen can diffuse from remote locations (Ref. 162).

8.1 Cracking Morphology

Hydrogen Induced Cracking involves two basic forms - straight cracks and step-wise cracks (Ref. 154) - generally related to an alloy's microstructure.

A blister initiating at a manganese sulphide inclusion may propagate as a crack through untempered martensite, bainite or even pearlite, in areas that would correspond to the segregation bands of an ingot (Ref. 80,133,134). In fact, high levels of elements, such as manganese and phosphorus, that would concentrate in the segregation bands have been found both in and around cracks (Ref. 133). In high strength steels, the cracks have been found associated with prior austenite grain boundaries similar to Sulphide Stress Cracking (Ref. 154).

Blisters tend to form in the pipe or vessel wall in areas comparable to segregation zones - near plate edges and centres, and in 1/4 or 1/2 thickness zones (Ref. 105,161). The hydrogen builds to high pressures (Ref. 124) and the blisters expand, frequently towards the inside against the system pressure (Ref. 56,74) but also to the outside (Ref. 124). Blisters have been found ruptured by cracks running from the blister centres to the surface of the component. In addition, a series of blisters has been found, torn open to form a chain of cracks. Blisters were also noted with cracks at their ends, perpendicular to the original direction (Ref. 124).

Step-Wise Cracking occurs when hydrogen blisters in different planes connect when the metal between them tears (Ref. 154) (Photograph 7). When two blisters approach each other, the hydrogen pressure within them creates stresses on the small metal ligament sufficient to cause plastic deformation (Ref. 79). If no external stress is applied, stresses high enough to create cracks will be located at the tips of the blister cracks in a step-wise direction (Ref. 131). If external stress is present, fracture is aided by the creation of a shear stress acting upon the manganese sulphide matrix interface to trigger opening, thereby accelerating hydrogen precipitation. Stresses high enough to cause cracking will be found at the blister flank when external stress is present and crack propagation will be through the material thickness (Ref. 131,154). (Also see crack morphology in Section 2, Glossary of Terms.)

There are many factors influencing the Hydrogen Induced Cracking susceptibility of steels. These can be classified as environmental variables and metallurgical variables.

8.2 Environmental Variables

It has been demonstrated, by both field and laboratory experience, that environmental variables have a profound effect on the response of an alloy to HIC.

8.2.1 Hydrogen Sulphide Concentration

In general, the response of an alloy to HIC will vary with the concentration of hydrogen sulphide; susceptibility to damage increases as the concentration increases (Ref. 153). There are indications that low levels of hydrogen sulphide may restrict damage by preventing the hydrogen level from reaching the threshold necessary to cause blistering and/or cracking (Ref. 26). This optimum hydrogen sulphide level is questionable as blistering has been encountered at hydrogen sulphide levels well below the NACE (Ref. 1) definition of sour environments (Ref. 1,55).

8.2.2 pH

The pH of test solutions and operating environments producing HIC, has been a point of controversy for many years. This subject was further complicated by the difficulty in calculating operating pH. Until recently, there were few instruments that could yield accurate field readings.

The BP Test (Ref. 165) uses a pH of 5.1 to 5.3 and under these relatively mild conditions alloying elements such as copper can produce protective films on the steel surface (Ref. 41,75,78). These films reduce the corrosion of the steel and, hence, the hydrogen available for charging. The Canadian Sour Gas Industry and the Heavy Water Industry, recognizing that corrosion activity increases with decreasing pH, have specified pH levels of 3.5 and 3.0 respectively (Ref. 142) in their test solutions. These lower pH values have resulted in severe HIC, in the form of Step-Wise Cracking, in steels that were relatively undamaged at higher pH levels. It is apparent that sulphide scales that are protective in milder solutions are dissolved in more aggressive environments.

Steel manufacturers have confirmed the increased corrosion activity and cracking at lower pH levels (Ref. 41,42). However, it was also determined that susceptible steels will not necessarily show significant differences in HIC with variations in pH. Poor steels will remain poor despite the pH, but resistant steels may show significant HIC if the pH is low enough (Ref. 55).

Recent measurements using pH meters in sour natural gas pipelines indicated values of approximately 5.5. The relatively mild conditions of the BP Test would be representative of the operating characteristics of this system. Additional studies will be performed on other lines to establish a data base for pH values under various operating conditions.

8.2.3 Temperature

Conditions most conducive to HIC involve temperatures of 5° to 40°C. Temperature variations between 15° and 35°C appear to have little effect on the

rate of HIC (Ref. 55). As temperatures rise above 40°C, HIC decreases, probably because the solubility of H₂S decreases or, because more stable sulphide scales are formed (Ref. 174,175). Certainly, if the temperature is raised to the 125°C region a stable sulphide scale is produced, reducing corrosion rates to low levels (Ref. 174).

8.2.4 Solution Contaminants

Solution contaminants, such as dissolved chlorides and carbon dioxide, probably contribute to the corrosivity of the solution by generating more hydrogen on the surface of the metal. This has been confirmed by experiments which show that synthetic sea water produces higher corrosion rates than water solutions with a similar, or lower, pH (Ref. 41). In addition, tests have confirmed that synthetic sea water solutions with a pH of 3.5 to 4.3 caused higher corrosion rates, greater hydrogen absorption, and more cracking than pure water solutions with a similar pH (Ref. 171). These higher corrosion rates might be expected as chlorides present in the sea water solutions, have a propensity for pitting, thereby perforating any scales that may have formed.

Similarly, dissolved carbon dioxide is considered to increase the severity of the corrosive environment (Ref. 171). In fact, it is felt that 5% NaCl saturated with a mixture of 1.03 MPa partial pressure of H₂S and CO₂, is more severe than the NACE test solution (Ref. 41).

Carbon dioxide contributes to the severity of a liquid environment since dilute acids form when CO₂ dissolves in water. The acids increase the corrosion rates of the steels, generating more hydrogen. Analysis of the gas in blisters found in a natural gas pipeline revealed some 2.4% carbon dioxide (Ref. 138). Significant traces of carbon dioxide were found in other cases (Ref. 74) confirming that contaminants must be considered in the design of any system.

8.3 Metallurgical Variables

Metallurgical variables are perhaps the most important consideration in the selection of steels to resist HIC. Solution parameters are largely decided by natural factors such as the gas field or process chemistry. Therefore, testing has concentrated on manufacturing processes, heat treatments, and chemical compositions in an effort to develop steel resistant to HIC.

8.3.1 Casting Practice

One of the most important metallurgical factors influencing Hydrogen Induced Cracking of steel is the segregation of impurities and alloying elements during casting. Segregation of impurities leads to concentrations of non-metallic inclusions and these are favoured sites for the initiation of HIC (Ref. 35,76,154). In addition, segregation of alloying elements tends to result in banded structures with a resultant high hardness and a propensity to crack and/or blister (Ref. 80,133,134).

HIC tests are designed to make steels crack. The extent of the damage is then assessed and is related to the expected performance in the field. Samples are chosen from areas of the plate or pipe most prone to attack (Ref. 7,142). At times, making this selection of samples can be quite difficult as susceptibility to HIC often varies between ingots in a heat. This variation depends on "cropping" practice and on the temperature of the finish-rolling.

The effects of the casting method are disputed with some indications that there are no differences in HIC between continually cast and ingot cast material (Ref. 26). However, continuous casting as used in small ingot heats for piping (Ref. 137), might be preferred in order to obtain inclusions in a narrow zone away from the surface (Ref. 7,28).

8.3.2 Deoxidation Practice

Deoxidation practice has been investigated on numerous occasions but the conclusions vary. Early papers tend to recommend full killing with silicon and aluminum to produce structures more resistant to hydrogen blistering and cracking (Ref. 124). More recent investigation has suggested that semi-killed steels are much more resistant to HIC (Ref. 7,43, 133). This resistance may result from the elimination of alumina particles which have been identified as initiation sites for HIC (Ref. 75,154). In addition, the semi-killing tends to leave the non-metallic inclusions in a spheroidal shape (Ref. 133) so that they are not elongated during rolling. Consequently, the inclusions are less likely to capture hydrogen. In contrast, sulphides in fully-killed steels, solidify as thin films in the austenite grain boundaries and between dendrites (Ref. 7,55).

8.3.3 Microstructure

It is generally considered that susceptibility to HIC in steels is highest in what are termed discontinuous and/or banded structures (Ref. 75,80,119,133). Cracks tend to initiate at elongated manganese sulphide inclusions, propagating along the low transformation structures of bainite and martensite (Ref. 42). As indicated earlier, analysis has revealed high concentrations of manganese and phosphorus in and around cracks. Such concentrations are consistent with segregation. Isolated islands of untempered martensite apparently cause no problem as long as they are below the 30% level normally considered necessary for cracking (Ref. 107).

8.3.4 Heat Treatment

Heat treatments of various types are employed to reduce susceptibility to HIC. The choice of heat treatment depends on the structure of the steel. For instance, although tempering at 650°C (1200°F) has been found helpful in reducing the HIC susceptibility of acicular ferrite structures, it was ineffective for banded pearlite structures (Ref. 173). Quenching following tempering is necessary to impart resistance to a banded structure (Ref. 173).

Although quenched and tempered steels are reported to be the structures most resistant to HIC (Ref. 137,153), the ideal structure appears to be finely dispersed spheroidized carbides in a ferrite matrix (Ref. 150). Normalized and tempered structures, although they cannot equal the HIC resistance of the ideal, are considerably more resistant than untempered martensite (Ref. 150, 153).

8.3.5 Controlled Rolling

Heat treatments associated with rolling operations may be of limited benefit. Temperatures reached during controlled rolling do not produce HIC-resistant, quench-and-tempered structures (Ref. 42). However, it may be the elongation of non-metallic inclusions due to the controlled rolling, rather than the heat treatment, that makes the steel more prone to HIC attack.

Controlled rolling is generally considered to be detrimental to steels containing normal levels of sulphur (Ref. 142). With ultra-low sulphur material, controlled rolling does not have an apparent effect (Ref. 134) probably because there are fewer non-metallic inclusions to be elongated in the process.

Manganese sulphide inclusions appear to be more easily elongated as the rolling temperature decreases (Ref. 134). However, if some residual strain, not exceeding 10%, can be introduced into the plate, HIC can be reduced (Ref. 134).

Cold rolling or other forms of cold working, such as straightening, can have either a beneficial or a detrimental effect. Severe cold rolling (over 20% deformation) markedly increases the HIC susceptibility of steels while less than 20% appears to have a beneficial effect (Ref. 176). Furthermore, in cold tensile deformation, maximum benefit with respect to HIC appears at about the 5% level (Ref. 176). However, other research indicates a substantial detrimental effect with as little as 2% cold working (Ref. 177). Since the effects of cold working are not clear, it might be better to employ stress-relieved components.

8.3.6 Nonmetallic Inclusions

Nonmetallic inclusions are generally accepted as the prime initiation sites for HIC (Ref. 42,80,119,135). Manganese sulphides are normally considered as those most often associated with hydrogen defects as they tend to be long and to be associated with segregation zones (Ref. 7). However, there is increasing evidence that alumina particles (Ref. 75,154), glassy silicates and complex carbonitrides (Ref. 26,43) also act as prime sites for the initiation of blistering and HIC.

Inclusions tend to be elongated in the rolling direction and, consequently, present their longest dimension to the diffusing hydrogen. Hydrogen collecting at these points produces the blisters associated with HIC (Ref. 63). Spheroidal inclusions are not easily elongated by rolling and, therefore, are not very susceptible to hydrogen collection (Ref. 7).

Lowering the sulphur content of the steels is considered a major method of combatting HIC in that the number of manganese sulphides would be reduced.

However, there is little agreement on the sulphur levels required to make a steel resistant to HIC. Laboratory testing has indicated the absence of HIC with sulphur levels below 0.002% (Ref. 28). Many other studies have concluded that HIC will still occur with sulphur levels as low as 0.001% (Ref. 2,43,137). Lowering sulphide levels does not seem to be an effective means of eliminating HIC.

8.3.7 Shape Control

It is generally agreed that elongated inclusions which possess large surfaces and sharp edges are the shapes most vulnerable to HIC (Ref. 7,28). Rounded inclusions, due to their more perfect geometrical shapes, are not as susceptible to hydrogen collection and/or to deformation during rolling. Therefore, shape control of inclusions, in combination with low sulphur content, is considered as a feasible means of reducing susceptibility to HIC (Ref. 76,78).

Shape control has been attempted by making additions to the ladle. Perhaps the most successful has been calcium in finely dispersed powder (Ref. 75,76,78,112,171). This resulted in spheroidization of the inclusions with very limited HIC under extremely severe test conditions (Ref. 142).

Rare Earth Metal additions have been reported to be very successful in preventing HIC (Ref. 177). Contradictory studies indicate that HIC initiates at Rare Earth Metal sulphides rather than at manganese sulphides in tested alloys (Ref. 107). In addition, the severity of the test medium can have a great effect, as Rare Earth Metal additions did little to improve HIC resistance in Heavy Water Industry tests at a low pH (Ref. 142). However, Rare Earth Metal additions with titanium have resulted in globularization of inclusions and may hold promise (Ref. 131).

Cerium additions have proved somewhat beneficial in spheroidizing manganese sulphides. However, clusters of nonmetallic inclusions may still occur, resulting in the initiation of HIC (Ref. 134).

8.3.8 Alloying Elements

Next to controlling the number and shape of inclusions, alloying elements have received the most attention in attempts to develop materials resistant to HIC.

Copper as an alloying element to prevent HIC has been studied extensively, particularly by the Japanese. It has a beneficial effect upon HIC resistance under certain pH conditions (Ref. 2,51,79,133,141). The benefit is thought to be derived from the formation of a surface film in conjunction with mackinawite. This film reduces the corrosion rate and, hence, the hydrogen available for charging. Also, copper may reduce hydrogen diffusivity in the steel (Ref. 154).

Copper is effective only in relatively mild solutions with a pH above 4.8 (Ref. 142,171), although there is some indication that a pH as low as 4.5 may be acceptable (Ref. 124). The beneficial effect of copper may be improved by adding about 1% Cobalt (Ref. 129). The pH of the environment may be lowered to a range

of 3 to 3.5 without encountering HIC. Under these conditions the copper apparently helps to prevent hydrogen absorption, again through a film-forming mechanism. Aluminum, tin, and titanium may also improve the HIC resistance of a copper-bearing steel (Ref. 41).

Not all elements added with copper have been beneficial. For example, 0.1% molybdenum added to copper-bearing steels increases the general corrosion and also the susceptibility to HIC (Ref. 171,173) probably because the molybdenum retards film formation. Similarly, nickel additions of 2% or more and 0.1% tungsten to copper-bearing steels have also increased HIC susceptibility (Ref. 41), although the nickel's effect is questionable (Ref. 171).

The addition of known poisoning agents such as selenium and tellurium to copper-bearing steels, seems to increase the hydrogen absorption rate without increasing the corrosion rate. The level of HIC does not change as a result of these additions (Ref. 41).

Copper in steels that are subjected to cathodic charging is apparently ineffective in preventing HIC even under mild solution conditions (Ref. 28). The hydrogen charging prevents formation of a protective film. In low pH solutions, copper additions to the steel should be avoided as they result in increased general corrosion rates (Ref. 142).

Manganese in alloys may increase the resistance of the steel to HIC but this effect may depend on the pH of the testing or operational environment. In low pH environments, the presence of 0.8% to 1.8% manganese has been found to increase the severity of HIC (Ref. 42). In more moderate environments, the presence of greater than 1.8% manganese apparently reduces the susceptibility to HIC (Ref. 173). This result would be consistent with the formation of a surface scale. However, manganese levels as high as 4% are reported to have little, or only a slight negative, effect upon HIC (Ref. 171).

Nickel, as in the case of Sulphide Stress Cracking, appears to be somewhat controversial in its effect on HIC. In general, the presence of up to 1% nickel seems to decrease hydrogen absorption by the steel (Ref. 171, 173). In combination with copper, the addition of nickel retards HIC (Ref. 147). However, these effects are most commonly encountered in solutions with a pH above 5.0 (Ref. 119) and are consistent with a film formation. Other tests suggest that nickel can be beneficial with solutions of pH 3-5 (Ref. 131). Alloying elements, in addition to nickel, may have produced some of the beneficial effects noted. There is also ample evidence to suggest that nickel added to copper bearing steels may impair the benefits of the copper (Ref. 42,171). Again, solution composition and severity greatly influence the test results.

At any rate, nickel additions greater than 1% are avoided to prevent the formation of structures prone to SSC.

Cobalt, like nickel, is a controversial alloying element. There are some indications that 0.5% cobalt can reduce hydrogen absorption significantly but the effect becomes consistent only above the 1.0% level (Ref. 42). In

conjunction with copper, cobalt at levels over 1.0% reduces the HIC susceptibility of steels in an aggressive environment with a pH of 3.0 to 3.5 (Ref. 42). Lower levels of cobalt, added with copper, appear to have no significant effect in improving resistance to HIC (Ref. 171).

Chromium is said to have a positive effect on the HIC resistance of steels as it lowers the overall corrosion rate (Ref. 118). In levels up to 0.3%, chromium has been found effective in reducing HIC in synthetic sea water (Ref. 177). Similarly, chromium levels up to 0.6% were found quite effective in lowering hydrogen absorption, particularly if the pH was over 4.8 (Ref. 42,119), and the alloy contained up to 0.3% copper (Ref. 42). Since high chromium levels can result in structures prone to SSC, a balance in chemistry must be attained.

Other Elements - There are a number of other elements that have been examined for their effect on the HIC resistance of steels (Ref. 171). Test results may be summarized as follows:

- (a) additions having a beneficial effect upon the reduction of HIC:
Bismuth 0.08%, Rh 0.02% and Pd or Pt 0.08%
- (b) additions having a negative effect:
Y up to 0.5%, Zr or Hf up to 0.08%, Si up to 0.8%,
Ta up to 0.08%, Ir up to 0.08%, Al up to 0.32% (Aluminum used to deoxidize steels is present at levels often exceeding 0.32%. Consequently, HIC susceptibility of these steels probably is increased.)

8.4 Measuring the Effects of Hydrogen Induced Cracking on Service Life

Testing for HIC is generally performed in laboratories on relatively small samples. The samples are immersed in the test medium and corrosion, with resultant hydrogen charging, occurs from all sides. In the field, hydrogen charging occurs from only the process side so that hydrogen diffusing through the pipe wall is able to escape, lowering the levels in the metal (Ref. 6,41,45). If the level of hydrogen can be lowered below that required for blistering and/or cracking, the component will continue to operate without experiencing HIC problems (Ref. 41,45).

To reflect field conditions, the laboratory test can coat all but one side of the immersion samples, so that charging occurs from one side only (Ref. 100). This results in lower HIC damage than would be the case with all-sided charging. Steels which perform poorly under all-sided charging may prove to be acceptable with one-sided charging (Ref. 79). Even so, correlation with field experience is questionable as the HIC damage appears to be still somewhat higher in laboratory conditions.

Testing of full-size pipe samples with the environment on the inside only, simulates field conditions (Ref. 29,166). Hydrogen charging takes place from one side and pressures can be utilized to reflect operating conditions. Cracking damage may be monitored during testing with ultrasonics (Ref. 166) or even by acoustic emission (Ref. 179). In addition, the hydrogen passing through

the wall may be monitored with suitable probes, permitting calibration of the amount of hydrogen necessary to produce cracking.

Full-size pipe testing, has established that a hydrogen gradient exists across the sample thickness (see Figure 8.2). Cracking will occur if hydrogen levels reach the threshold values for cracking. Since elongated stringers are most likely to occur at mid-wall thickness, it has been postulated that blistering and/or cracking cannot occur if the hydrogen level, at this mid-wall point, is below that required to create a blister (Ref. 40, 45, 115, 154). Testing of various steels using hydrogen probes on the outside surfaces can determine the hydrogen diffusivity values required for cracking to occur.

Since correlation has been poor between all-sided charging in tests and one-sided charging in field conditions, attempts have been made to reconcile the results through an assessment of crack damage using ultrasonic C-Scan techniques. Test conditions involved the relatively mild BP solutions. Samples encountering a Crack Sensitivity Ratio (CSR) of 30% during all-sided charging experienced no cracking in a one-sided test approximating field conditions (Ref. 166). Consequently, material that performs poorly in the laboratory may be, in fact, quite acceptable under field conditions.

Minor hydrogen damage may occur in steels. Removal of protective scales by erosion may create conditions of hydrogen charging that lead to cracking without propagation to failure. Re-application of the protective scale, either intentionally through pre-conditioning or accidentally in normal operations, can reduce the rate of hydrogen diffusivity below the level required to cause further damage. Consequently, material containing hydrogen-induced defects may continue in service, but the safety of the components is questionable.

Burst tests on full-size piping samples that had undergone HIC tests in the laboratory revealed degradation of the pipe properties (Ref. 166). In the case of severe damage, rupture may result at pressures below those usually necessary to cause yielding. Weeping of the solution might also be expected at blisters (Ref. 124) as the material thickness is effectively reduced in these areas.

In another test, a vessel that had suffered hydrogen blistering in service was subjected to a destructive hydrostatic test. It contained numerous blisters and one of the blisters was the site of a crack that constituted failure under the test. The crack occurred when the yield point was slightly exceeded; the increase in circumference was only 0.3%. The hoop stress at bursting was 248 MPa (35,800 psi) versus 310 MPa (45,000 psi) for undamaged material (Ref. 124).

It seems apparent that care must be exercised in the application of hydrostatic testing to equipment that has been subjected to mild HIC conditions. Minor damage could be induced to propagate into large cracks by stresses generated during the testing and these cracks might progress to failure under operating conditions.

8.5 Summary

Hydrogen Induced Cracking occurs when monatomic hydrogen, produced by corrosion on the surface of the steel, penetrates and diffuses through the steel until it is trapped at naturally-occurring voids in the metal. The monatomic hydrogen collects in the voids, forming molecular hydrogen which builds pressure until the yield strength of the alloy is surpassed and blisters form. Blisters link to produce cracks when the intervening metal tears. This blistering mechanism does not require the application of external stresses.

8.5.1 Characteristics of Hydrogen Induced Cracking

Hydrogen Induced Cracking, generally initiating at non-metallic inclusions, displays the following characteristics.

- (1) Hydrogen Induced Cracking does not occur in weld metal.
- (2) There is a threshold level of hydrogen required to crack or blister a steel. Defects will not occur if the critical hydrogen level is not reached.
- (3) Blistering and/or cracking occur at elongated inclusions which are located in the segregation areas of the ingot.
- (4) Manganese sulphide inclusions, preferred sites for crack initiation, often are found in low transformation temperature structures, such as martensite and bainite.
- (5) The cracks and blisters usually occur parallel to the rolling direction but may form a "step-wise" pattern by tearing between blisters in different planes.
- (6) Cracks frequently occur in association with Sulphide Stress Cracking as both defects occur in areas of segregation.

8.5.2 Factors Affecting Blistering or Cracking

There are a number of variables that affect the Hydrogen Induced Cracking resistance of an alloy (see Figure 8.3).

- (1) Hydrogen Sulphide Concentration - The higher the concentration of hydrogen sulphide, the greater the susceptibility to damage.
- (2) pH - The lower the pH, the greater the susceptibility to damage.
- (3) Deoxidation Practice - Deoxidation with aluminum promotes HIC as alumina particles are active initiation sites for blistering. Semi-killed steels are more resistant to blistering than fully-killed steels since semi-killed steel contain fewer non-metallic inclusions and/or these inclusions are rounded in shape.

- (4) Controlled Rolling - Controlled rolling of steels tends to elongate the non-metallic inclusions and, consequently, to increase the HIC susceptibility.
- (5) Sulphur Content - Lowering the sulphur content to 0.001% drastically lowers the HIC susceptibility because the non-metallic inclusions are reduced in number.
- (6) Shape Control - Round inclusions are not likely to crack because they have an ideal shape and because they are not easily elongated during rolling. Calcium additions which promote appropriate shape control of the inclusions, particularly in low sulphur materials, greatly reduce the HIC susceptibility of an alloy.
- (7) Alloying Elements - Alloying elements are frequently added to the melt to help control HIC by preventing corrosion and, hence, the generation of hydrogen. Corrosion is reduced through a film formation. However, this effect occurs only under relatively mild conditions with a pH over 4.8.

Chromium, manganese and copper are all effective in preventing corrosion under mild environment conditions. However, manganese additions are not recommended as there could be an increase in manganese sulphide sites suitable for blister initiation. Copper must be used with caution, also, as it will result in increased corrosion at a pH below 4.5.

Nickel is reputed to have a positive effect upon HIC resistance. However, as it may promote hardening and subsequent Sulphide Stress Cracking, its use should be restricted to the 1% level.

8.5.3 Effect Upon Service Life

Hydrogen Induced Cracking may drastically reduce service life of components, particularly if damage is enhanced by frequent hydrostatic testing. High stresses created during testing can cause failure during subsequent operating cycles. Testing should be related to operating conditions.

Table 8.1

HYDROGEN DAMAGE RESISTANCE REQUIREMENTS FOR HYDROGEN SULPHIDE SERVICE		
Hydrogen Concentration Co / $\mu\text{g/g}$	Environment	Experience
2 - 6	Moist H ₂ S and O ₂ / 29°C, 310 kPa	CTR = 10 CLR = 34 / blistered within 12 months
1 - 6	Moist / Aqueous H ₂ S / 29°C, 310 kPa	CTR = 18 CLR = 58 / severely blistered after 2 months
		CTR = 9 CLR = 29 / not blis- tered after 6 months
3.5	Moist H ₂ S / 30°C, 3.1 MPa	CTR = 18 CLR = 34 / not blis- tered after 6 months
		isolated blistering in similar steel in identical service else- where
0.2	Aqueous H ₂ S / 30°C, 2.8 MPa	no blistering / non-corroding pipe
1.3	Aqueous H ₂ S / 80°C, 2.8 MPa	no blistering / corroding pipe

After Hay and Dautovich (Reference 142)

Table 8.2: Several Examples of Failure by Hydrogen Induced Cracking

No.	Location	Plant	Materials (Steel)	Used Conditions and Environment	Operating	
					Beginning Date	Failure Discovered
1	U.S.	Sour refinery (crude oil)	Mild Steel (Y.P. 28 kg/mm ²) (T.S. 42 kg/mm ²) C 0.23, Si 0.06, Mn 0.58 P 0.009, S 0.029, Al 0.009	Phillips Petroleum Co., Ltd. examples of blistered vessel: over 50 H ₂ S-H ₂ O, low operation pressure	unknown	unknown
2	Japan	Heavy oil desulfurization apparatus, condenser shell	Mild steel (SB42) C 0.18, Si 0.30, Mn 0.80, P 0.030, S 0.030	H ₂ S+H ₂ O 38 °C Operation pressure 48 kg/cm ²	5/1971	6/1973
3	Japan	Desulfurization apparatus	Mild steel (SB 42) Low alloy steel (1.25 Cr 0.5 Mo)	H ₂ S+H ₂ S 50 °C operation pressure 32 kg/cm ²	4/1966	8/1968
4	Japan	Desulfurization apparatus	Mild steel (SB42) C 0.17, Si 0.26, Mn 0.78, P 0.015 S 0.018, Cu 0.09	H ₂ S+H ₂ O (condensate) operation pressure 17.33 kg/cm ²	4/1964	9/1965
5	Japan	Desulfurization apparatus	Mild steel (SB42)	25-110 °C operation pressure 33 kg/cm ²	11/1961	8/1967
6	U.S.A.	Refinery vessel	carbon steel	Shell Oil H ₂ S, CO ₂ , NH ₃ , H ₂ O	---	1954
7	U.S.A.	Line pipe (Barkodon gathering)	API 5LX-52(24" x 0.271" t SAW) 1.75-1.95 cold worked	Elpaso Natural Gas Co. Ltd. Natural gas, CO ₂ 15%, H ₂ S 1%	1954	1954
8	FRG	Line pipe	API 5LX-42(ERW) annealed and straightened	H ₂ S max., 0.95%, CH ₂ 80-85%, CO ₂ 8.7% operation pressure 45.5 kg/cm ²	1/1961	1/1961
9	Italy	Refinery	Mild steel C 0.12, Si 0.26 Mn 0.47, P 0.017, S 0.018 API 5LS-65 as rolled	H ₂ S 10%, H ₂ 5% gasoline	unknown	unknown
10	Arabia (Persian Gulf)	Line pipe under sea (crude oil)		Crude oil (H ₂ S) + sea water	1972	1972
11	Arabia	Line pipe on land (sour gas)	API 5LS-X-42 as rolled spiral	H ₂ S 3.4 vol %, CO ₂ 8.8 vol%, CH ₄	1974	1974

After Ikeda and Kawaka (Reference 154)

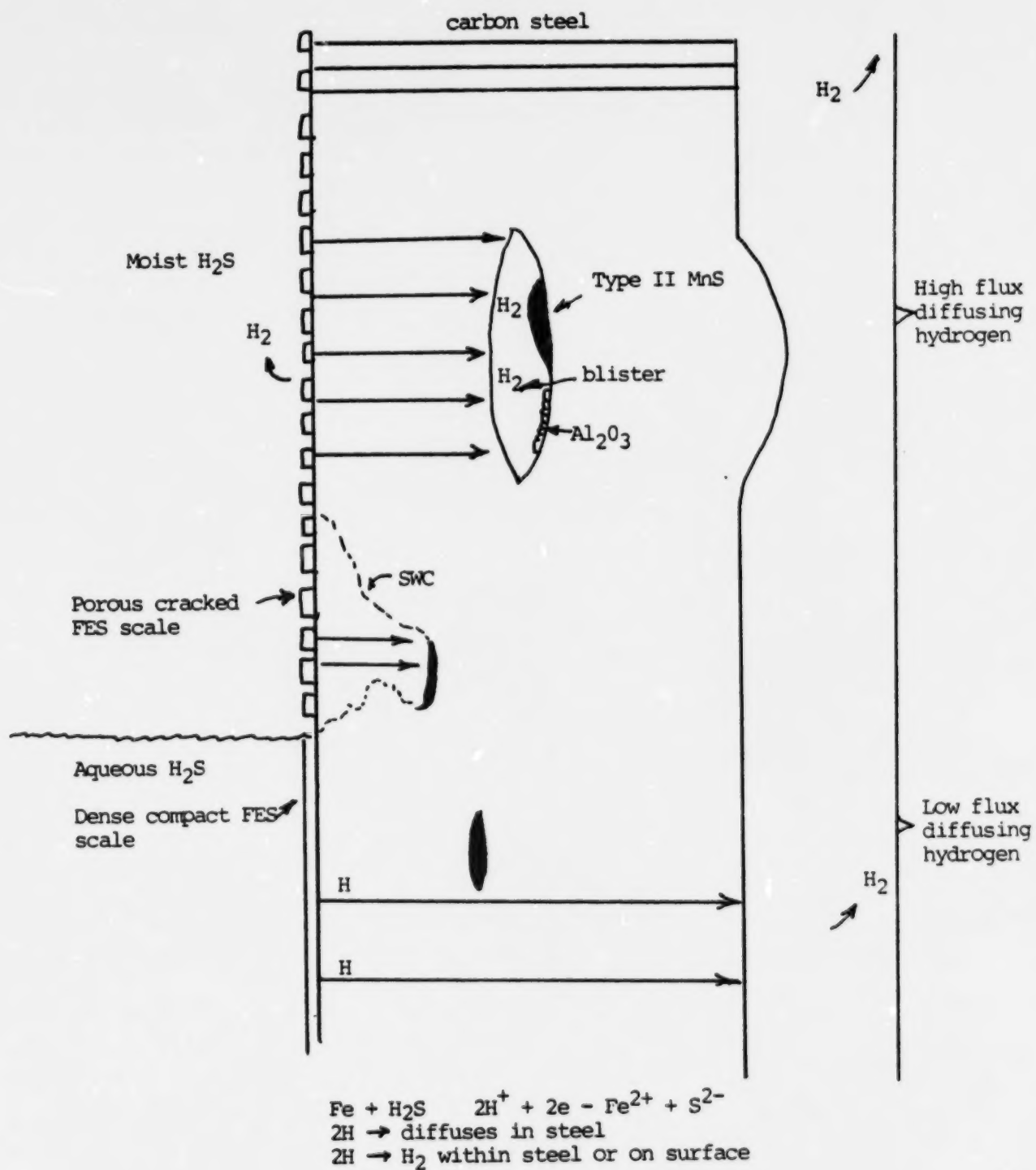


Figure 8.1: Schematic of HIC Under Heavy Water Plant Conditions

(From Hay, M.G., Reference 143)

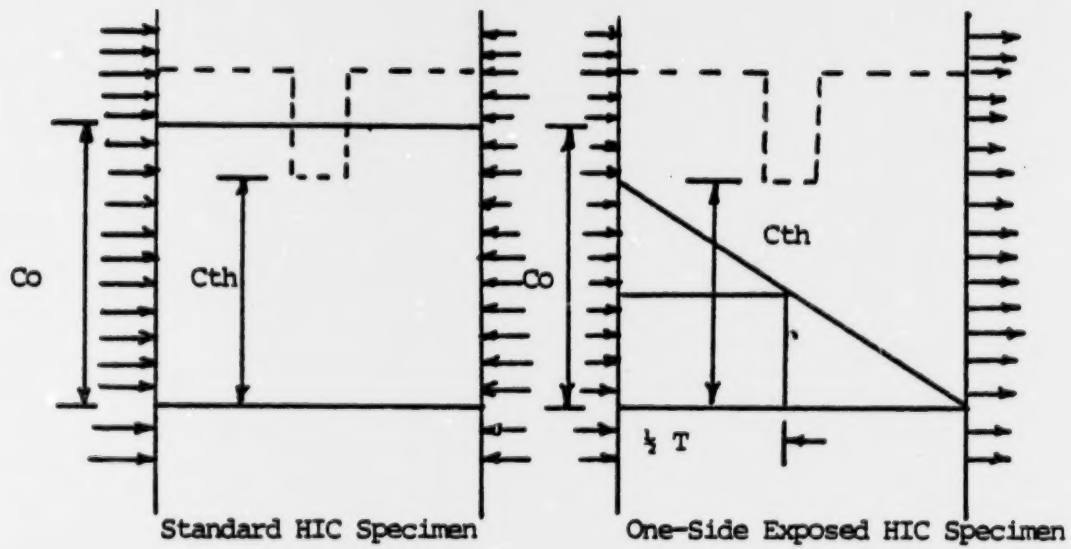


Figure 8.2: Hydrogen Concentration in Through-Thickness Direction in Standard and One-Side Exposed HIC Specimens

(After Taira et al, Reference 115)

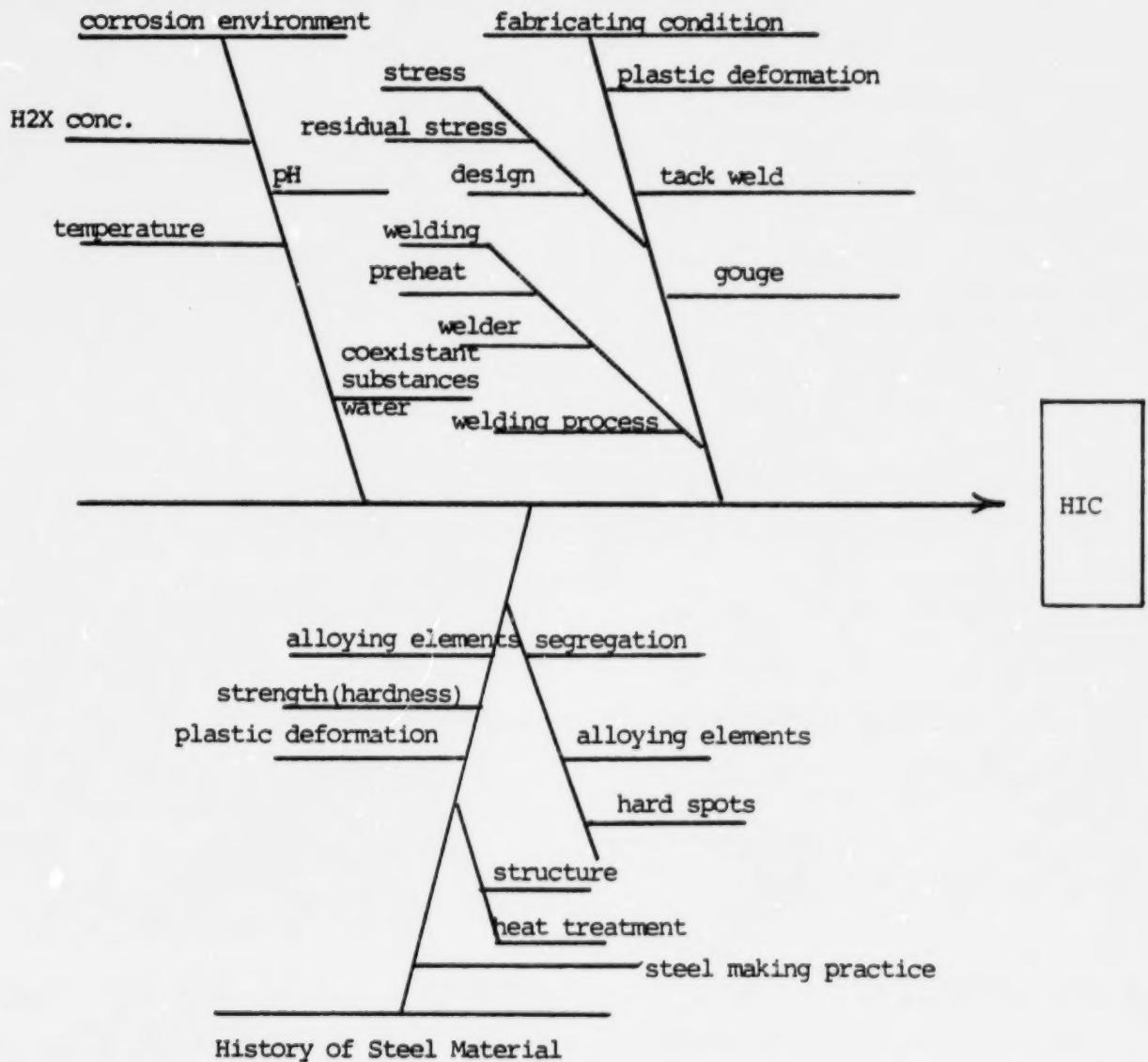


Figure 8.3: Factors Affecting Hydrogen Sulphide Induced Cracking
(After Ikeda and Kowaka, Reference 154 with some additions)

9. TESTS TO DETERMINE SULPHIDE STRESS CRACKING AND HYDROGEN INDUCED CRACKING

There are a number of test methods used to detect Sulphide Stress Cracking and, later, Hydrogen Induced Cracking. Solutions vary in concentration, pH, temperature, and dissolved components to simulate operating environments, but the basic test methods are unchanged.

9.1 Static Bend Test (SSC)

The static bend test involves loading a reduced material specimen as a cantilever beam. This technique avoids the difficulty of maintaining pure axial loading as can be encountered in a tension test.

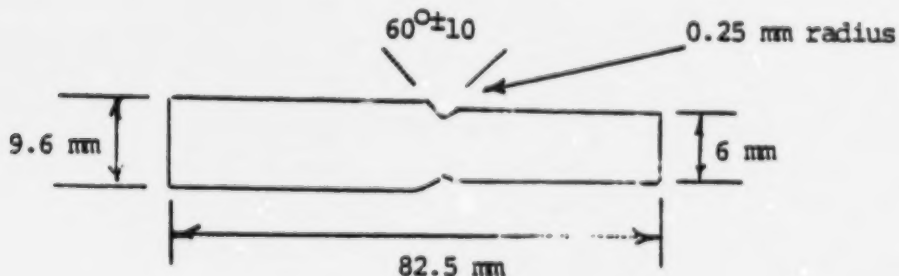
The sample, which may be a simple cylinder with a circumferential notch, is supported at one end while the other end is loaded by suspending weights from it. The weight may be moved along the specimen to provide the desired bending moment. Stress is calculated using the conventional cantilever beam formula:

$$\text{Stress} = \frac{MY}{I}$$

where M is the maximum bending moment

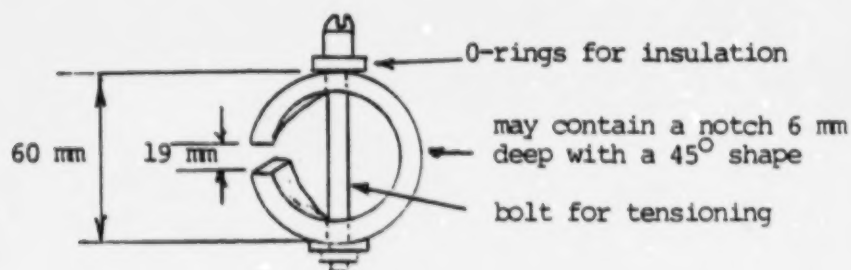
Y is the distance from the centre of the section to the outer fibres

I is the moment of inertia of the section.



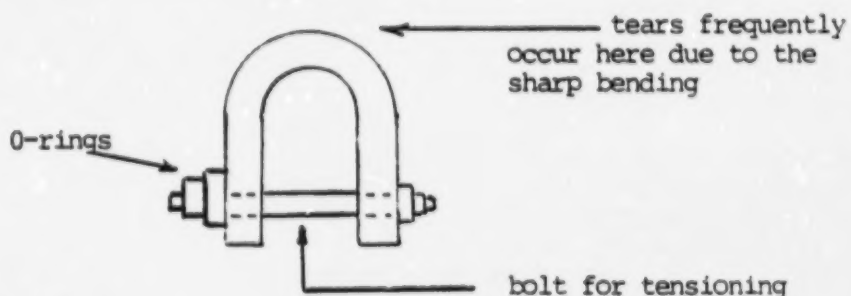
9.2 C-Ring (SSC)

As the name implies, the sample being tested is in the shape of a C with a bolt used to produce stress. The C-ring may or may not be notched. C-rings were originally chosen as test coupons because they could be manufactured easily from piping or tubing by simply removing a section. Unfortunately, the measurement of tensile stresses generated by tightening a bolt tends to be highly inaccurate.



The dimensions of the ring may vary to accommodate the pipe or tube diameter being tested.

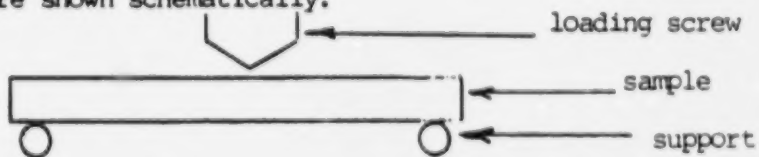
A variation of the C-ring, called the U-bend, involves bending material, usually plate or rod, to a fixed radius. Again, a bolt is used to provide the tension. Stresses in this coupon tend to be highly variable. The bending often leads to fissuring in the outer fibres, resulting in failures caused by mechanical considerations rather than corrosion ones.



9.3 Bent Beam Test (SSC)

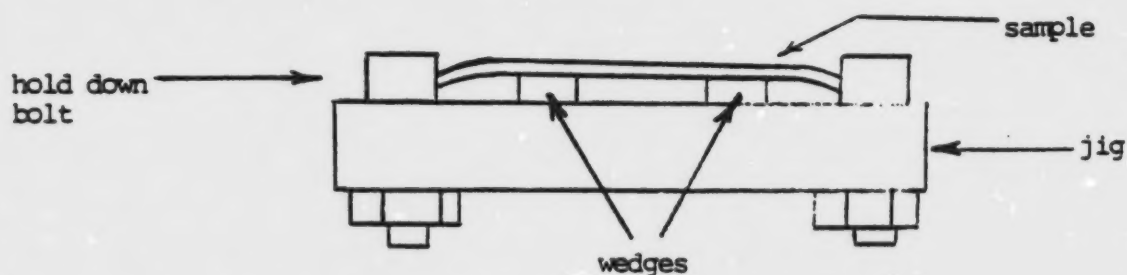
There are several bent beam tests. All employ the sample material as a simple beam supported at both ends and bent in the middle to create stress for the test. The samples are then immersed in the test solution for a fixed time period, frequently 30 days (720 hours).

Two examples of coupons are shown schematically.



The sample is generally 1.6 mm x 4.8 mm x 7.6 mm (1/16" x 3/16" x 3"). This test is frequently referred to as the Shell Bent Beam Test. A test holder is employed to hold the beam and to apply the load. Glass tubing is frequently used to prevent galvanic contact.

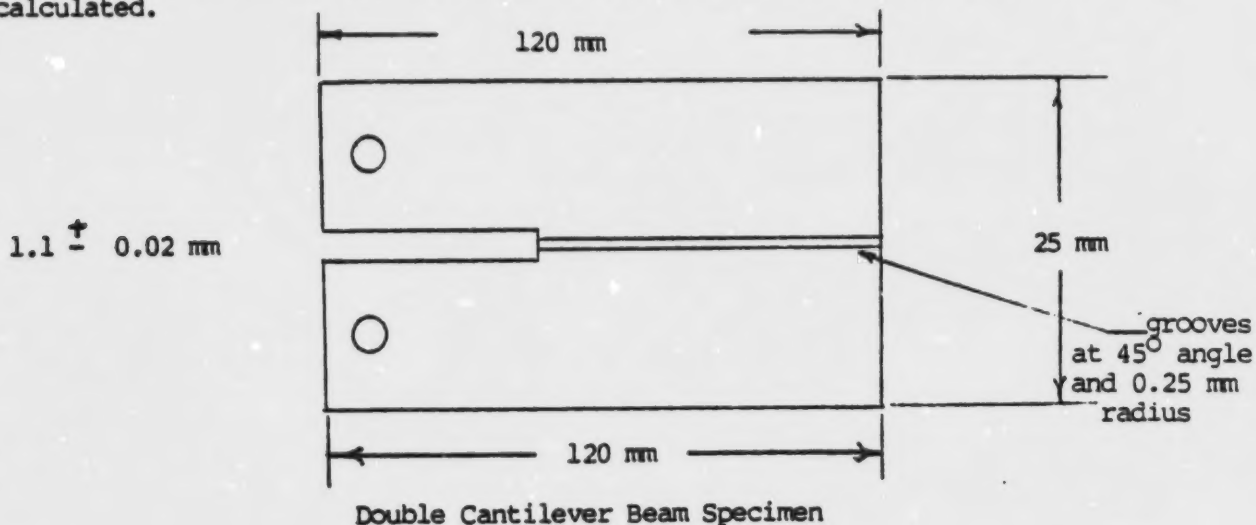
A variation of this test method involves loading the beam by placing wedges between it and a jig. The wedges can be varied in thickness to cause different deflections and, hence, different loads.



9.4 Double Cantilever Beam (SSC)

This method involves a fracture mechanics approach to determine the critical stress intensity for slow crack growth induced by the corrosive environment. The sample in the shape of a double cantilever beam, contains a carefully machined notch. The beam is loaded by inserting a wedge into the notch. The sample is then exposed to the test medium for varying periods, although 14 days is generally the minimum. Cracking may be continuously monitored by resistance measurements so that one knows when the cracking process for the given wedge load is complete.

Once cracking is complete, the coupon is cooled down in liquid nitrogen and then fractured. Alternatively, the sample can be torn apart at room temperature. The crack caused by the environment is readily visible as it is a characteristic dark colour versus the clean, bright metal of the newly fractured surface. The crack length can be accurately measured and the critical stress intensity factor calculated.



The dimensions may vary, but those shown represent the ones most commonly used.

9.5 Slow Strain Rate (SSC)

The Slow or Constant Strain Rate test is a form of simple tensile test. A smooth specimen, in the environment of interest, is pulled in tension at a constant strain rate until failure occurs. If the environment is non-aggressive, fracture occurs in a normal, ductile manner. Sulphide Stress Cracking markedly decreases the ductility of the specimen and, generally, results in the formation of secondary cracks near the main fracture.

Strain rate must be carefully selected. Too fast a strain rate will result in ordinary ductile fracture. Too slow a strain rate may not show the effects of SSC due to the formation of protective scales. SSC susceptibility may be described by time to failure, percent reduction in area, percent elongation, plastic strain to fracture, or energy absorbed prior to fracture.

Comparison made between materials tested in air at the same strain rates and those tested in the process environment is an additional method of assigning SSC susceptibility.

9.6 Hydrogen Induced Cracking (HIC)

Hydrogen Induced Cracking susceptibility testing involves the immersion of material coupons in the test environment for a fixed period, usually 96 hours. Immersion is followed by metallographic examination of polished sections to measure the amount of damage. As HIC is a primary concern, a typical testing procedure will be outlined in some detail.

9.6.1 Test Specimens

Test specimens are normally taken with the long axis parallel to the rolling direction of the plate or extrusion of the pipe. The specimens are chosen from three areas that are located at the 0, 90 and 180 degree locations (from the weld) in seam welded pipe and are equally spaced around the circumference of extruded pipe. Plate samples are normally chosen from edges but generally correspond with plate produced at the beginning, middle and end of each heat (to test for segregation).

The samples are generally 100 mm long x 25 mm wide and are of full material thickness up to a maximum of 25 mm. One mm may be removed from each surface to ensure that the surfaces are parallel and free from scale or other irregularities.

All six surfaces of each sample are generally finished to RMS 16. Side coating may or may not be permitted. Samples are degreased immediately prior to testing.

9.6.2 Test Solution

The composition of the test solution may vary considerably depending on the service environment. Solutions presently used, are outlined in Table 9.1. Testing should be carried out in a solution closely approximating the expected service environment with particular attention given to pH.

9.6.3 Test Procedure

The samples are stacked in a glass vessel, separated from one another by means of glass rods. They are covered with enough test solution to ensure a volume-to-surface area ratio of 3 ml/cm².

Nitrogen is used to purge the air from the solution and then hydrogen sulphide is bubbled through at the rate of one litre of H₂S per litre of solution, for one hour. The flow of hydrogen sulphide is then reduced to 10 ml per litre of solution for the duration of the 96 hour test.

9.6.4 Evaluation of Specimens

Following the testing, each sample is sectioned perpendicular to the long direction, at three locations: 25 mm, 50 mm and 75 mm from one end. The sections are polished metallographically. Examination may be carried out on unetched or etched surfaces, depending upon the examiner's preference.

Generally, examination is carried out at 50 to 100x magnification. Photographs are often taken for reference. The true lengths and the true thicknesses of all cracks are determined (see HIC Terminology, Section 2). Damage is then assigned as:

- | | |
|-----------------------------|-----|
| (a) Crack Length Ratio | CLR |
| (b) Crack Thickness Ratio | CTR |
| (c) Crack Sensitivity Ratio | CSR |

Acceptance of a material is based on assignment of CLR, CTR, and/or CSR of cracks in the operating environment. Caution must be exercised, however, as this test is designed to make material crack. Consequently, acceptance must be based on defined crack levels as zero defects in harsh environments are not practical.

Table 9.1: Test Solutions

Test Method	Test Solution	Period	Evaluation	Comments		
HIC	BP Type	Synthetic Seawater saturated with H2S at room temp. pH 5.1-5.3	96 hrs	cracks/diffu-sible hydrogen blisters	Used by most tests referred to in this report.	
	NACE	0.5% acetic acid +5% NaCl saturated with H2S at room temp. pH 3.5-3.8	96 hrs	cracks/diffu-sible hydrogen blisters		
	CSA Sour Gas Proposal	0.5% acetic acid +5% NaCl saturated with H2S at room temp. pH 3.5	96 hrs	cracks/diffu-sible hydrogen blisters		
	BHWP	0.5% acetic acid +5% NaCl saturated with H2S at room temp. pH 3.0	2-96 hr periods	cracks/diffu-sible hydrogen blisters		BHWP and AECL tended to use this.
	New NACE Proposal	Synthetic Seawater saturated with H2S at room temp. pH 4.8-5.4	96 hrs	cracks/diffu-sible hydrogen blisters		Objected to by Heavy Water Industry and Canadian Sour Gas Industry. NACE T-1F20 Proposal
SSC	NACE Tension Test	0.5% acetic acid +5% NaCl saturated with H2S at room temp. pH 3.5-3.8	720 hrs	Ratio of Thres-hold strength to yield strength	NACE T-1F-9 Proposal	
	Shell Bending Type	0.5% acetic acid saturated with H2S at room temp. pH 3.5-3.8	720 hrs	Sc value when Sc=critical stress in Ksi units x 10		
	C-Ring Specimen	0.5% acetic acid +5% NaCl saturated with H2S at room temp. pH 3.5-3.8	up to 30 days			
	Cathodic Charging	Any applicable solution although 4-5% H2SO4 is commonly used.	variable	cracks/hydro-gen diffusion blisters		

10. CASE HISTORIES

In order to outline the effects of hydrogen sulphide on alloys used in industry, a series of case histories has been assembled. These case histories generally involve failures, rather than successes, to illustrate the damaging effects of the environment. They have been arranged in three sections - problems in the Heavy Water Industry, problems in the Sour Gas Industry, and problems in the Refining Industry.

10.1 Heavy Water Industry

As outlined earlier, the environment of heavy water plants involves either moist gaseous hydrogen sulphide or gaseous-aqueous solutions saturated with hydrogen sulphide at relatively low temperatures and pressures. The temperatures of the cold sections, 30°C, are ideal for both Hydrogen Induced Cracking and Sulphide Stress Cracking. However, other considerations such as erosion/corrosion must also be addressed.

The following material outlines some of the damage reported at various locations.

10.1.1 Pitting

The flare header in the Glace Bay Heavy Water Plant (Ref. 83) suffered relatively rapid attack due to fouling by corrosion products. The corrosion products retained moisture from a water seal overflow and from a stack steaming operation. The corrosion products also acted as a dam to hold water in the line. Also, the line had been sloped in the wrong direction during construction, so that the seal overflow ran down the line away from the stack, rather than to the drain.

Rapid pitting corrosion was experienced below the liquid level with indicated rates of 1.8 to 3.3 mm (70 to 130 mils) per year. A through-wall pit occurred after 12 months service.

Examination of the line revealed large, randomly oriented pits displaying the characteristic "oyster shell" pattern usually associated with hydrogen sulphide attack in stagnant conditions (Photograph 1).

Pitting also occurred in the type 304L stainless steel heat exchanger tubing. The pits, varying from relatively shallow to through-wall, were randomly oriented. Type 316L material in the same service showed only minor pitting.

10.1.2 Erosion/Corrosion

Erosion/corrosion, in the Heavy Water Industry, is used to describe a form of attack that removes the protective sulphide scales from the steel surface, exposing the underlying metal to high rates of corrosion.

Erosion/corrosion occurred at the Glace Bay Heavy Water Plant in several two-pass heat exchangers (Ref. 83,85). Stainless steel sealing strips on the

longitudinal baffle were damaged, probably during installation. By-passing of the seals set up high localized flow conditions, removing the iron sulphide scales on the exchanger shell and tubesheet in the baffle areas. Rapid corrosion proceeded and perforation occurred at the junction where the shell thickness decreased to 28 mm from 51 mm. Service life was 14 months.

The heaviest attack occurred at the inlet end of the shell and tapered off towards the floating head (the higher pressure differential was at the inlet end). Large, smooth-sided depressions were created, the sharp contours indicative of erosion (Photographs 8,9,10).

Hydrogen generated by the above-mentioned corrosion penetrated the shell, producing small internal blisters about 0.75 to 1.0 mm in size. These blisters, or delaminations, associated with non-metallic inclusions, were completely isolated (Photograph 4). No linking or Step-Wise Cracking pattern was found.

10.1.3 Hydrogen Induced Cracking

Hydrogen Induced Cracking was found in various pieces of equipment at the Bruce Heavy Water Plant. The cracks originated at pre-existing laminations, at type II manganese sulphides, and at alumina particles (Ref. 141, 142, 143). The cracks, displaying a Step-Wise pattern, had occurred after service lives varying from two months to several years. This variation was related to the severity of a component's environment. Tightly adherent sulphide scales did not prevent hydrogen entry and damage.

It was determined that moist hydrogen sulphide gas resulted in a much higher hydrogen flux in steels than did an aqueous solution. Consequently, damage in the gaseous environment was more probable. This was confirmed by laboratory test results.

Exhaustive laboratory studies revealed that steels could be classified as to crack damage, using a Modified BP Test with a solution pH approximating the worst condition anticipated, should an upset occur. By establishing limits for CTR and CLR, steels could be selected to resist cracking in such environments as moist hydrogen sulphide gas and oxygen at 29°C and 310 KPa, and moist hydrogen sulphide gas at 30°C and 3.1 MPa (Ref. 98).

10.2 Sour Gas Industry

The Sour Gas Industry involves "downhole" situations, pipeline systems and plants. The equipment can be quite diverse and complicated. Pipeline failures have prompted a flurry of investigations into the effects of hydrogen sulphide on steels and information is generally available in groups of reports from the 50's and 60's. However, with the failure of a line in Saudi Arabia in 1974 (Ref. 7), the rash of work generated has continued without abatement. Consequently, a great deal of new information is available, along with some classic case histories from the past.

10.2.1 Hydrogen Blistering (Ref. 74)

In 1950 the El Paso Natural Gas Company installed a 600 mm (24") trunk line with 400 mm (16") and 200 mm (8") laterals from a gas field to a treatment plant. The gas contained 15 mole % CO₂ and 1 mole % H₂S. From October 27, 1951 to January 1952 four breaks occurred in the 600 mm (24") line and six breaks occurred in the 400 mm (16") lateral. Blisters were associated with all the breaks.

An analysis of the gas in the blisters indicated that it was 94% hydrogen, 2% methane, with traces of carbon monoxide and carbon dioxide. Hydrogen blistering was identified as the cause of failure.

All the line failures originated in blisters and most of the blisters broke to the inside of the pipe, against the gas pressure. In all breaks the pipe ripped at two places 180° apart, usually at the three o'clock and the nine o'clock positions. The breaks followed a sinusoidal curve and passed through welds with the symmetry being broken only when the rip went through other blisters. All indications pointed to sudden brittle fracture.

10.2.2 Blistering and Cracking (Ref. 7)

In 1974 three separate service failures occurred in a spirally-welded API 5LX Grade 42 sour gas transmission line. Failures occurred four to seven weeks after commissioning. All the failures were due to Step-Wise Cracking associated with elongated manganese sulphide inclusions. Blistering was often, but not always, evident in the cracked areas.

The failures were always located near the spiral weld but were never identified with weld defects. The blistering and cracking were randomly located at the bottom and sides of the pipe, never in the top quadrant. Cracking was not observed in the weld or heat affected zone.

The mechanical properties of the pipe were deemed to have no effect upon the failure.

The steel making practice - using aluminum and silicon deoxidation coupled with controlled rolling to form long thin Type II manganese sulphide inclusions - was deemed responsible for the formation of blisters and/or cracking.

10.2.3 Lamination and Blistering (Ref. 138)

A welded, natural gas line of 400 mm O.D. and 9 mm wall thickness made of plain carbon (0.22C) steel burst after four months service. The line, 12 km long, operated at 60 atmospheres.

The pipe was found to have a black internal film and large, flat blisters. Ultrasonic examination revealed numerous other laminations where no blisters were evident. Only butt welds and their adjacent areas were crack free.

An analysis of the gas in the blisters revealed:

89.4% H ₂
2.4% CO ₂
7.0% N ₂
1.7% O ₂

It was postulated that the nitrogen and oxygen were present due to air entry during testing and the hydrogen content was actually 97.4%.

The cracks were "Step-Wise" in nature and generally originated at blisters in the centre-line of the pipe. The number of defects decreased as examination of the pipe moved away from the gas entry point.

A section of pipe, hydrostatically tested, could be raised to 1 1/2 times operating pressure without trouble. Rupture occurred in a highly blistered region soon after the pipe passed the yield point, about 170 atmospheres.

10.2.4 Cracks in Weld Area (Ref. 164)

Two failures occurred in Westcoast Transmission Company's Grizzly Pipeline in British Columbia, in July, 1981. The pipe was Grade 359 spiral weld 508 x 9.5 mm. Operating life to failure was 17 months with 27.5% H₂S natural gas at a pressure of 6-7 MPa. Fractures occurred in the weld and heat affected zone.

All cracks were associated with the spiral welds and fell into three categories:

- (1) cracks in weld metal transverse to the weld direction,
- (2) cracks in weld metal parallel to the weld direction,
- (3) cracks parallel to the welds in the heat affected zone.

Cracks in the heat affected zone were found to have some "Step-Wise Cracking" tendencies. These were most evident in the middle third of the pipe wall. No hardening of the heat affected zone was found except for one spot.

Failure was attributed to Sulphide Stress Cracking in the weld face and in the heat affected zone in material that was generally less than Rc 22 in hardness. It was felt that stresses and environment were extremely severe, causing failure of a normally resistant steel. Sulphide Stress Cracking propagated through enough of the wall to cause rupture of the remaining metal in mechanical overload.

Perhaps testing of some welds might be in order as submerged arc welding can produce welds prone to SSC under certain conditions. In addition, Treseder (Ref. 153) has reported that RB 93 is the limiting hardness to prevent failure in some automatic, submerged arc welds.

10.2.5 Inhibitors (Ref. 12)

During the initial four years of operation, a natural gas pipeline experienced

eight leaks through pitting, due to water and accumulated sludge. Inhibition was employed with varying success.

The variable success was probably the result of continual changes in inhibitors. If the initial system had been balanced and left alone, it is likely leaks would have been avoided.

10.2.6 Oil Industry Tubulars (Ref. 90)

Six case histories of failures in well tubulars and other drilling equipment indicated that failures were encountered due to hardnesses above Rc 22 in parts of the equipment. The high hardness stemmed from such things as poor or non-existent heat treatment, mechanical damage during straightening, and/or hard spots produced by local quenching during manufacture.

10.2.7 Sulfinol Contactors, Amine Contactors, Vessels (Ref. 56)

After eight years of service, hydrogen laminations were found in a sulfinol primary contactor built in 1966. Two areas of laminations, 360 x 910 mm and 250 x 1000 mm, were identified. Holes, drilled into the areas from the outside, were fitted with gauges to monitor hydrogen activity. Ultrasonic examination was carried out on the shell at 6 month intervals to monitor progression of the defects.

An amine contactor (A-type Scrubber), constructed of A 212 FBQ of varying thickness and designed to scrub H₂S from natural gas, experienced blistering in a 100 mm (four inch) thick section just above the liquid level. The blisters were large with one about 1600 sq mm. The inside surface, bulging about 6 mm, contained a circumferential crack 100 mm long. Ultrasonic inspection revealed areas of segregation.

During preheating to repair the vessel, 50 new blisters appeared. The vessel was repaired by venting the blisters, welding plate on the outside, gouging out the blisters and filling them with weld metal. A 316 stainless liner was applied on the inside.

A second vessel of A516 Grade 70 developed blisters after two years and a 1.85 metre section was replaced.

Hydrogen blistering in an inlet chiller separator was discovered along the top centre of the horizontal component after approximately four years service. The vessel was constructed of A516 Grade 70 material. Blisters were up to 150 mm in diameter. Ultrasonic examination showed extensive laminations. Ruptured blisters were repaired by welding and vent holes were drilled from the outside to the area of segregation. The interior of the vessel was coated with epoxy as a temporary measure.

10.2.8 Amine Contactor (Ref. 73)

Three amine/sour gas treating contactors suffered blistering and step-wise cracking in periods ranging from 10 months to three years. The blisters were

found in areas where high corrosion had occurred. Other areas of the vessels were protected by heavy scales. Erosion due to boiling had removed the protective scales, exposing the metal to corrosion.

10.3 Refining Industry

Although conditions in the refining industry are somewhat different to those in either the Sour Gas or the Heavy Water Industries (see Section 3), failures due to hydrogen sulphide still occur.

10.3.1 Blistering in Various Vessels (Ref. 124)

Embrittlement and blistering were encountered in equipment handling sour crude, sour crude fractions, sour natural gases and gasolines. Blisters varied in size from 3 mm up to 300 mm x 600 mm (1/8" up to 12" x 24"), the number of blisters varying from plate to plate. The blisters were frequently encountered in bands in the steel and were generally parallel to the rolling direction.

Blisters were drilled and the gas was analyzed as 99.5% hydrogen. Sometimes sparks from the electric drill ignited the gas, causing violent explosions.

Five blisters that developed in a refinery vessel were tapped and the gas pressure measured. Values of 6.89, 11.71, 17.22, 18.60 MPa (1,000, 1,700, 2,500 and 2,700 psi) were recorded. The maximum operating pressure in the vessel was 7.86 MPa (270 psi) and 2.79 MPa (405 psi) during hydrostatic testing.

A natural gasoline vessel that had been removed from service and then filled with gas at 205 kPa (30 psi) ruptured. The vessel failed along the knuckle radius of one head. Blisters along this knuckle radius had torn open to form a discontinuous chain of cracks along the failure line. The blisters tended to be parallel to the rolling direction and bulged to both the inside and outside surfaces. Cracks were frequently found at blister edges, at right angles to the original blister direction. (Was this the start of Step-Wise Cracking?)

Impact tests showed fibrous results and it was postulated that segregation of phosphorus had occurred with blistering concentrating in the segregation band. Large inclusions or small strings of inclusions, were also considered as prime areas for blister formation. It was felt that many of the blisters occurred at laminations that had not been closed by rolling. (This is now discounted.)

A blistered vessel was tested to destruction to determine whether or not embrittlement had occurred. The vessel was 600 mm (24") in diameter x 2.29 metres (7.5') long with a shell thickness of 4.76 mm (3/16") and had been used as a make-up, tank water leg in a sour, natural gasoline plant. It contained numerous, closely-spaced blisters up to 50 mm (2") in length.

Under test, the vessel leaked at a 11 mm (7/16") crack at the edge of a blister. The yield point had been only slightly exceeded as the increase in circumference was 0.3%. The hoop stress at bursting was 246.66 MPa (35,800 psi) versus 310 MPa (45,000 psi) for an undamaged section. No embrittlement was detected.

10.3.2 Cracking of Carbon Steel Welds (Ref. 167)

A light ends fractionation unit designed to process hydrocarbon feeds containing up to 2% by volume of hydrogen sulphide, suffered cracking of hard weld deposits in four major carbon steel pressure vessels after three weeks in service.

The most heavily damaged vessel contained three cracks (based upon visual examination). The longest crack was 280 mm (11") long and extended approximately 127 mm (5") on either side of the weld. The other two cracks were 25.4 mm (1") long and were in the weld deposit.

Internal inspection revealed 300 cracks, all transverse, and all contained in the submerged arc weld deposits. Closing head welds made by manual metallic arc contained no cracks.

Two other vessels by the same manufacturer also had cracked welds.

Chemical analysis revealed manganese and silicon contents twice the level allowable by the ASME Code. Hardness readings were 235 to 255 BHN. Piping and other vessels welded with MIG and submerged arc also showed higher hardness than the allowable but had had a manual arc stringer or back weld, preventing the cracking.

Welding Procedures for the submerged arc process permitted the use of filler metal and flux known to produce high manganese and silicon, both of which contribute to high hardness.

Micro hardness tests showed areas with hardnesses over 300 BHN. These hard areas and those with high manganese and silicon contents did not respond to conventional heat treating procedures.

Hardness surveys on other vessels indicated that many submerged arc welds and some MIG welds exceeded the hardness limit of BHN 235. These welds usually contained high levels of manganese and silicon.

10.3.3 Blistering of Drum (Ref. 126)

An overhead drum suffered hydrogen blistering and pitting due to 2.0 to 4.2 mole percent of hydrogen sulphide in the streams. The temperature was approximately 37.8°C (100°F) with a pressure of 68.95 kPa (10 psig). The vessel was lined with Monel and both a filming inhibitor and a neutralizing inhibitor were used to control the attack.

10.3.4 Blistering of Vessel (Ref. 37)

Extensive damage to steel equipment through hydrogen blistering and fissuring can be sustained when streams which contain ammonia and hydrogen sulphide at a pH of 7-9, are processed.

An accumulator fabricated from A70 FBQ plate was removed due to severe blistering after five years of service. Blisters measured up to 75 mm (3") in

diameter and 11 mm (28/64") deep in 25.4 mm (1") plate. Three blisters were drilled and the gas analyzed. In each blister, the gas was 99% hydrogen.

Bend tests indicated that embrittlement had occurred and it was suggested that trapped molecular hydrogen was responsible.

10.4 Summary

Case histories amply outline problems associated with sour environments. These problems involve hydrogen blistering and/or cracking, sulphide stress cracking, pitting and erosion/corrosion.

Cracking usually occurred in components due to high hardness, particularly in the heat affected zones of welds. Cold working, introduced during straightening, also created structures prone to cracking.

Normally, Hydrogen Induced Cracking resulted in rupture as blisters linked together in a discontinuous chain. Analysis of the gas in blisters indicated concentrations of hydrogen in excess of 97%. Blisters were identified as originating at manganese sulphide inclusions, particularly if these inclusions were elongated.

Quality assurance methods were stressed as being critical in the production of equipment capable of resisting sour gas environments.

11. MATERIALS OF CONSTRUCTION

Although NACE MR-01-75 is in general use for the selection of materials for sour service, there are many instances in which materials recommended may fail due to the fact that the service environments deviate from those used to test candidate alloys. In addition, operating plants and facilities have developed material lists, based on experience, that are frequently used to augment the specifications. Fortunately, the results of some of the testing and material recommendations are available for inclusion in this report (Ref. 21,120,123, 140,146).

General guidelines, applicable to virtually all installations, would include the selection of fine-grained carbon steels with a maximum hardness of Rc 22 in both the parent material and welds. However, some thought might be given to using RB 93 as the maximum hardness in welds, particularly if the environment is severe. This will require some form of postweld heat treatment, probably a stress relief, to ensure compliance with this requirement.

Some attention should also be given to the forming operations. Controlled rolling of normal sulphur steel may result in the elongation of manganese sulphides, thereby promoting Hydrogen Induced Cracking. Similarly, the killing chemistry might be considered as alumina particles also have been found to act as nucleation sites for blistering.

A number of other general considerations might involve the restriction on the use of copper alloys and cast irons which are subject to both excessive corrosion and crack sensitivity. Control of velocities to levels of 2.1 to 3.0 metres/sec to reduce erosion/corrosion, or the use of higher alloys when the velocities cannot be reduced, should be considered.

A number of specific tests and recommendations are made in the following subsections. Many papers outline tests carried out on numerous alloys, particularly by individuals and by laboratories establishing the limits of materials listed in MR-01-75. Only a few tests and recommendations are described for the purpose of review and comparison.

11.1 Alloys Resistant to Sulphide Stress Cracking

Laboratory and field tests were conducted on C-ring specimens of a variety of alloys for resistance to Sulphide Stress Cracking and general corrosion (Ref. 123). The alloys were required to provide resistance to Sulphide Stress Cracking under the following conditions:

- (a) a 0.2% offset yield stress,
- (b) with 13.6 J (10 ft-lbs) minimum and 20.3 J (15 ft-lbs) average full size transverse Charpy V impact strength at -57°C (-70°F), and
- (c) a minimum 0.2% offset tensile yield stress of 413.7 MPa (60,000 psi).

Alloys meeting these conditions were listed as:

- (1) AISI 4340 (Quenched and Tempered, 26 Rc).
- (2) Vulcan Steel Astralloy (Quenched and Tempered 25 Rc).

- (3) Inco K-Monel (Mill annealed and age hardened, 29 Rc).
- (4) A 286 (Solution annealed 982°C (1800°F) and Aged 718°C (1325°F) at the mill, 32 Rc).
- (5) Titanium Alloy 6 Al -4V (Mill annealed to Rc 26).
- (6) J&L304N (Cold worked by Mill to Rc 26).
- (7) Armco PH, 13-8 Mo (Supplied by Mill in annealed condition, heat treated to condition H 1150 M, 30 Rc).

Alloys not meeting the test requirements included Armco 15-16 WR, Uniloy 326, Ebrite 26-1, Vaculoy 26-1, Armco 18-2 Mn, Armco 22-13-5, Custom 445, and Custom 450.

While the tests indicated the success of certain alloys, others suggest that Armco PH 13-8 Mo (Ref. 172) and K-Monel (Ref. 21) should be used with caution.

11.2 Valves

Valves, always a source of concern in the sour gas industry, were the subject of the materials specifications NACE 1F-166, and, subsequently, MR-01-75.

Failures in valves tend to occur for a variety of reasons (Ref. 21).

Valve stems of K-Monel material have failed in service. The hardness levels were generally above the Rc 35 recommended by MR-01-75. In fact most valve component failures can be assigned to hardness levels above those recommended by specifications. For example, welds on a valve bonnet were Rc 41 in the heat-affected zone and failed due to SSC. Valve seats of 13% chrome have cracked in service because hardness was above Rc 22. The same can be said in failures of Guide and Drive pins where hardnesses of Rc 41 have been noted.

In short, it appears it is absolutely essential to have a good quality assurance program in place to check manufacturers (Ref. 21). Unique procedures and specifications may be needed with each valve manufacturer to ensure that his product will meet the requirements of sour service (Ref. 140).

11.3 Sour Service Bolting (Ref. 21,91)

Stud bolts and nuts are particularly important as they can be subjected to severe conditions and their failure can result in the release of hazardous material. Yet, without exception, equipment manufacturers tend to exercise no control over their supply of these products and all too often studs are found with hardnesses beyond the maximum allowed (Ref. 21).

Studs for sour service are generally supplied to ASTM A193 B7M with a hardness limit of Rc 22 or BHN 235 to avoid SSC. Problems arise when suppliers attempt to heat treat B7 studs to modify them. Generally, they use 620°C (1150°F)

without considering the prior history of the product. The harmful martensitic and bainitic structures, not fully tempered by this treatment, can cause Sulphide Stress Cracking failures.

Hardness measurements on the products can also be misleading as they are performed only on one end, generally on a percentage sampling basis. 100% sampling appears to be justified, considering the consequences of failure (Ref. 91).

Crack detection (Ref. 91) might also be considered, at least on a sampling basis, to avoid unpleasant surprises.

11.4 Summary

Materials for sour service should be specified to recognized standards such as NACE MR-01-75 (latest revision). Hardness levels should be controlled to a maximum of Rc 22 in both welds and parent material to prevent cracking, although some thought should be given to a maximum of RB 93 in welds if high stresses are present.

Quenched and tempered structures should be obtained through proper heat treatment. This may involve the production of pilot heats to ensure that proper temperature levels and quenching are obtained.

Unique procedures may be required to ensure that manufacturers can provide products resistant to sour environments.

12. INSPECTION AND QUALITY CONTROL

Throughout the references, and particularly in the case history reports, the establishment of material quality assurance and equipment inspection programs is stressed as being of prime importance in preventing premature failure. The purpose of these programs may be as simple as ensuring that all components meet established standards (such as MR-01-75), or as complicated as assisting vendors to upgrade their products to comply with the requirements for sour service (Ref. 140).

Quality assurance is probably one of the least understood but most often used terms in industry. It is, however, only a term used to describe a formal system for managing quality control activities and it is only as good as the time, effort, and capabilities of the personnel involved.

The guidelines outlined in this section are derived largely from the author's experience in the petrochemical, refining and heavy water industries.

A Quality Program can be divided into two sections - one involving new components, and the second involving the examination of components in the field during operation and shutdowns.

12.1 Program Requirements for New Components

The basis for most programs is a Quality Assurance, Quality Control, or Quality Verification, Manual, depending on the level of confidence required. Emphasis is placed on written procedures and specifications in order to avoid future disagreements. Regardless of the product or service, a number of essential parameters must be established for a quality program:

- (1) a quality assurance department independent from design, production, maintenance, or marketing functions,
- (2) standards of quality that reflect the needs of the customer, the characteristics of the manufacturing process, the desired in-service performance, the safety of plant personnel and the requirements of legislative bodies,
- (3) written procedures covering all phases of design, production, inspection and installation with a program for continuous review and updating,
- (4) regulations for the control of documents such as specifications, change orders, inspection tickets or reports, shipping releases, and drawings,
- (5) a means of identifying parts which will permit tracing any component during construction and, later, in service,
- (6) a method for timely detection and segregation of nonconforming material and a program for corrective action.

- (7) schedules for the periodic calibration of inspection tools,
- (8) creation of files to retain essential documents and files,
- (9) programs for the training and qualification of key inspection personnel,
- (10) systems for control of manufacturing and construction including establishment of key inspection points, and
- (11) a system for periodic audit of any or all of the above steps by persons not directly involved in the manufacture or construction of the system being audited.

Even so, since problems will still arise in the design and construction of components, shop inspection or, at least, surveillance is a necessity.

12.1.1 Vendor Surveillance

Shop surveillance should involve some elements of inspection to ensure a complete and thorough investigation of potential problems. Relying upon the manufacturer to control his processes can have disastrous results. For example, someone, measuring inaccurately, could record the correct figure, yet the component would not fit when it arrives at site. It is too late to inspect quality into a component after it is built.

In addition, certain construction and fabricating practices, while acceptable in other circumstances, may create havoc in hydrogen sulphide service. Excessive straightening after stress relief, gouges and tool marks (Ref. 90), or interruption of a heat treat cycle, may all lead to in-service cracking.

Vendor surveillance should be carried out by personnel directly responsible to someone at the operating facility. All too often, construction problems are ignored and left to operations personnel to correct. Similarly, exceptions or deviations from specifications may be granted by project personnel who, interested in completing a contract, may not consider the consequences of the changes. Problems with equipment in a sour gas field (Ref. 157) could have been avoided through proper Quality Control with no deviation from procedures.

Shop surveillance should include the witnessing of hydrostatic tests, hardness tests, leak tests, ultrasonic inspection, and performance tests. Radiographs should be examined and correlated with a visual examination of the weld to ensure that all surface irregularities are indicated. More than one failure has been avoided by the discovery that some poor welds had been overlooked during radiography.

Welding procedures and practices, as well as consumables, should be monitored to avoid conditions leading to high concentrations of manganese and silicon.

12.1.2 Ultrasonic Scanning of Plate

All plate used for pressure vessels and welded piping should be examined at the mill for laminations and other defects. The preferred technique involves scanning 100% of one major side of the plate with a normal probe, using ultrasonic flaw detection equipment. The scan should be made in parallel paths, ensuring a minimum of 10% overlap on each pass to provide full coverage. Acceptance should be to ASME Section V SA435 level II, rejecting defects not contained in a 25 mm diameter circle. Standard practice which accepts defects that can be contained in a 75 mm diameter circle, could lead to Hydrogen Induced Cracking under Heavy Water Plant conditions as indicated below.

Size of Pre-Existing Defect

		0	25 mm	Up to 76 mm
Hydrogen Concentration of steel surface	1 μ g/g	no effect	slight if any effect	no data
	2 μ g/g	no effect	no data	serious effect
	3.5 μ g/g	no effect	no data	serious effect
	6 μ g/g	no data	no data	serious effect

After Dautovitch et al (Ref. 140)

Similarly, all seamless piping should be mill-scanned for defects.

Laminations and other defects falling within the acceptance criteria should be located on a defect map to permit monitoring in service.

12.1.3 Hardness Testing

All welds and heat affected zones of vessels and piping destined for sour service should be subject to hardness testing in the fabricating shop or in the field. Welds should be tested after post weld heat treatment. The tests should be conducted on the process side whenever possible. If this is not possible, a simulated weld specimen should be made as part of the qualifying procedures. This test should employ the same welding consumables and technique as the original joint. Hardness tests would then be performed on the test weld. Metallographic sectioning of the test joint would permit a microhardness traverse. Subsequent testing of the field joints could then be performed on the external portions of the welds.

Hardness tests should be carried out on each 1.5 metres, or portion thereof, of longitudinal seams. For automatically welded pipe, tests should be performed at both ends of every section.

Circular seams should be tested according to diameter, with one test for each 120 mm of diameter up to a maximum of eight tests. Tests should be spaced evenly around the circumference.

12.1.4 Welding

Welding is probably the most tested fabrication step carried out in industry today. It is also the one that can experience the most problems.

All welding consumables should be held in quarantine until welding tests can be performed. These tests should involve the preparation of a joint that should then be subjected to the NDE requirements of the finished product (such as hardness, microstructure, impact, tensile, chemical analysis, ultrasonics, and radiography).

Postweld heat treatment of some sort is necessary on all welds destined for sour service. This heat treatment depends upon the alloy and may involve stress relief, solution annealing or even quench-and-tempering.

100% radiographic inspection should be carried out on all welds for sour service following postweld heat treatment. Acceptance to the ASME Code is generally required. Corner welds may be examined by a combination of radiography and ultrasonics but the purchaser's representative should witness this testing.

12.2 Plant Program

Most plant programs are termed Corrosion Monitoring Programs. Unfortunately, this term is now synonymous with ultrasonic thickness readings on piping during plant operation but a comprehensive program should involve both onstream and shutdown inspection using all non-destructive evaluation techniques and some destructive ones. The techniques should, of course, be suitable to the process and conditions being investigated.

12.2.1 Corrosion Monitoring Program

Corrosion monitoring programs generally involve ultrasonic thickness measurements at preselected points on piping and pressure vessels. Normally, readings are taken once a year through windows cut in the insulation (on insulated pipe and equipment). Spots for readings are located on the piping and equipment by accurate measurement or by paint spots if temperature and material compatibility permit. This ensures that readings will be taken at the same locations in future years to detect decreases in thickness.

All points are located on isometric sketches to permit re-identification where necessary and to also permit the detection of erosion patterns.

Points are selected by inspection, design and process personnel considering well-known factors. Some of these factors are:

- (a) a history of failure,
- (b) a change in process flow direction, such as at elbows,
- (c) a change in velocity, both upstream and downstream of flow restrictions, such as orifice flanges, valves, and reducers,

- (d) changes in material specifications,
- (e) areas of temperature change,
- (f) areas around rotating equipment,
- (g) areas of two-phase flow,
- (h) areas where acid gases can condense,
- (i) points at the liquid level lines in two-phase flow,
- (j) stagnant areas,
- (k) areas identified as prone to stress corrosion cracking,
- (l) areas where heat tracing could cause boiling, and
- (m) dissimilar metal welds.

As well, points are assigned on a line diameter basis but length and complexity of the line must be considered. Points are usually about 3 metres of pipe length apart if there is no reason to suspect abnormally high corrosion rates.

Minimum Number of Points

- (1) Lines 50 - 150 mm (2" - 6") should have 2 points.
- (2) Lines over 150 - 300 mm (6" - 12") should have 3 points.
- (3) Lines over 300 - 600 mm (12" - 24") should have 4 points.
- (4) Lines over 600 mm (24") should have 5 points.

The corrosion survey sheet should be quite detailed. A sheet proposed for the refining industry is attached for reference.

Many corrosion monitoring programs are employed to look for onstream line thinning only. Consequently, Sulphide Stress Cracking and Hydrogen Induced Cracking are totally ignored. However, through a sampling process, these defects may be identified before they become serious problems.

Sulphide Stress Cracking is normally associated with welds. By removing insulation, if necessary, in the vicinity of the welds at test points on elbows, and on welded pipe, ultrasonic flaw detection can be employed to search for cracks. Small elbows may be examined completely. Five percent of the test points in areas susceptible to Sulphide Stress Cracking should have larger sections inspected each year with flaw detectors. This would involve the removal of insulation in a band around the pipe or vessel.

Radiographic examination, augmenting the thickness reading survey, should be used to explore areas of indicated high corrosion on gas pipes. In addition, five percent of the weld regions near test points should be examined radiographically each year to check for cracking. Points that are radiographed need not be tested ultrasonically.

Similarly, areas where the possibility of HIC exists should be checked by flaw detectors for laminations, pits, and the presence of potential step-wise cracking. Again, five percent of the points should have extra areas uncovered to permit extensive investigation. Radiography also should be used at five percent of the points to verify thickness readings and to search for other potential problems.

Radiography and ultrasonics are considered the most valuable NDE methods to detect problems in gas plants, gathering systems and refineries (Ref. 5,12). However, acoustic emission was also identified as a possible tool used in the detection of hydrogen embrittlement (Ref. 179).

Electromagnetic induction and flux leakage detection with a Linalog tool have proved quite valuable in the sour gas industry (Ref. 5). This procedure, using gas or liquid pressure, propels an instrument through a line. The instrument contains both magnets to induce a flux and detectors that can identify any flux leakage at metal loss locations. The magnitude of the flux leakage is directly proportional to the metal loss.

The system is accurate and relatively fast. However, it is confined to straight runs of pipe, and the presence of non-conducting scales can distort the results. In addition, magnetic components of the instrument have experienced Sulphide Stress Cracking due to the sour nature of the environment.

The hydrogen probe also holds great promise for use in sour environments. Probes attached to the outside of pipelines have indicated successfully the hydrogen activity within the material and may be used to predict the cracking susceptibility of the steel (Ref. 11,36,92,142,162,178). Although, experience in other facilities suggests that probes were less useful (Ref. 5,157), design and/or poor maintenance could have contributed to the poor performance of these installations. There has been enough positive experience to suggest that the hydrogen probe should be part of any inspection program in an operating facility containing moist hydrogen sulphide gas.

Direct measuring devices such as corrosion coupons and test spools may also be used to advantage. Corrosion coupons, particularly from retrievable installations, have been used successfully in sour environments (Ref. 5,113,178) despite the fouling that is frequently encountered. The coupons offer the advantage of testing the same materials as the pressure envelope and the luxury of having a permanent record, provided the corrosion rate is not so excessive as to destroy the coupons.

Accurate measurements can be made of general corrosion through weight loss. Pitting can also be determined through direct measurement with a gauge.

Corrosion spools have indicated some interesting results, confirming the formation of protective scales (Ref. 113). They have the advantage of representing the actual flow characteristics and heat transfer conditions of a pipeline. In addition, they contain the fluid so one-sided hydrogen charging is occurring rather than coupon immersion with all-sided charging.

Electrical resistance thickness measurements can be valuable in indicating corrosion at a given instant. However, instrument sensitivity is not always adequate (Ref. 113). Similarly, Polarization Resistance Probes, although ideal for indicating corrosion occurring at the moment of testing, are severely restrictive as they may be used only in continuous electrolytes (Ref. 113,178);

conductive scales can bridge the insulator between electrodes, giving false readings.

Visual inspection is probably the most accurate and effective method of inspection. Pit gauges, calipers, and rulers all can be used to determine equipment and piping condition quite rapidly. Unfortunately, this method is confined to the outside of components while onstream, but it is particularly valuable during a shutdown.

Onstream inspection should involve a visual examination for leakage, vibration, insulation damage and broken or missing supports. An infrared scan, provided the operating temperature is above 100°C, can be utilized to detect poor insulation and even thin spots in equipment.

12.2.2 Proposed Onstream Inspection Program

- (a) Ultrasonic thickness readings, using digital equipment, should be carried out at all test locations. Frequency of inspection will depend upon corrosion rates.

<u>Corrosion Rate</u>	<u>Survey Interval</u>
0-0.1 mm (0-5 mils) per year	36 months
0.1-0.4 mm (5-15 mils) per year	12 months
greater than 0.4 mm (15 mils) per year	6 months

15% of the 0-0.1 mm (0-5 mils) per year corrosion rate stations should be surveyed randomly, at 12 month intervals. If any change in process or operating conditions takes place the survey should be performed at 6 month intervals until the new corrosion rate is established.

Ultrasonic flaw detectors should be used to explore suspicious areas for signs of pitting, lamination, or hydrogen blistering. In addition, 5% of the digital readings should be verified with a flaw detector during each survey period.

C-Scan equipment, if available, may be used to monitor HIC.

- (b) Radiography should be used (on gas lines) to verify high corrosion rates or to confirm defects identified by other methods. A random 5% of all monitoring points in hazardous service (e.g. gas lines) should be examined with radiography during any given survey.
- (c) Corrosion coupons and replaceable corrosion spools should be used in all systems to measure corrosion rates. Coupon installation should be of the retrievable type to permit onstream monitoring. Coupons should also include stressed samples for Sulphide Stress Cracking studies.

- (d) Resistance Polarization Probes and Electric Resistance Probes should be used in each major system as applicable. Probe readings should be taken once per month, or more frequently if high rates of attack are noted.
- (e) Hydrogen probes should be used on every major system. Hydrogen diffusivity should be established for each major system and should be correlated to screening tests for the alloy, to determine the propensity to HIC.
- (f) Visual examination should be carried out at least once a month, noting items such as leaks, misalignment, vibration, external corrosion particularly at the test points.

12.2.3 Proposed Shutdown Inspection Program

- (a) Visual inspection should be carried out on the internals of vessels and piping whenever equipment is opened. Frequency will depend upon the severity of the service but probably should not go beyond three years for large vessels.

Valves should be removed to allow access to piping with mirrors, boroscopes, fibrescopes, pit gauges and calipers. In addition, selected valves from potentially high corrosion rate areas should be completely disassembled to permit visual examination of all components. Failing this, the valves should be radiographed to reveal hidden problems.

10% of all accessible welds should be examined by liquid penetrant or magnetic particle, particularly in areas where prior history suggests potential problems. In addition, these welds should be subjected to a hardness test, both in the weld metal and heat-affected zone. Care should be taken to remove the hardening effects of the test for cracks have been known to start in such areas.

Representative studs from insulated joints should be removed for testing.

- (b) Ultrasonic inspection should be carried out on lines that were too hot to allow inspection during operation. This inspection should involve both flaw detection and thickness measurements.
- (c) Radiography should be carried out on liquid lines after they have been drained. Radiography should also be carried out on 5% of onstream test locations on liquid lines subject to Sulphide Stress Cracking and Hydrogen Induced Cracking conditions.
- (d) To avoid the possibility of lowering a material's tolerance to operating pressures, hydrostatic testing should be used cautiously (Ref. 124,138,166).

Leak testing using operating pressures, soap solutions, or sensitive gas systems such as helium, should be employed instead.

- (e) Neutralization of all systems containing austenitic stainless steel components should be ensured, either with ammonia or, preferably, with a carbonate wash.
- (f) Care should be exercised to ensure that all protective scales remain intact during equipment outages.

12.3 Inhibition Program

Inhibitors tend to form a very important part of any corrosion monitoring program, particularly in the sour gas (Ref. 5,12,89) and refining (Ref. 37) industries. As long as the inhibition is maintained, corrosion and cracking problems are avoided (Ref. 157), but if the inhibition feed rates are varied rapid pitting and/or cracking could result (Ref. 5,12).

Most of the inhibitors used in sour service are of the filming amine type (Ref. 12,35). They consist of molecules containing nitrogen ring compounds attached to a long chain hydrocarbon. The nitrogen is adsorbed on the metal surface and the hydrocarbon chain helps to make the surface hydrophobic.

Filming amines are generally ineffective in the absence of oil so water soluble inhibitors usually contain oil to make them viable.

Inhibition by filming amines appears to be effective at most pH levels. However, under conditions of hydrogen blistering some filming amine inhibitors, while reducing corrosion, actually promoted hydrogen entry into the steel (Ref. 35). Consequently, inhibitors should be tested in the medium in which they are expected to operate. It has been determined that the effectiveness of inhibitors may vary from gas field to gas field depending upon the composition of the environment.

Addition of inhibitors to systems may cause other problems related to production. Most organic inhibitors are surfactants and may cause foaming or emulsion problems. Also some inhibitors are very surface active and may cause loosening of protective scales. Therefore, extreme care must be exercised in any inhibition program.

12.4 Repair Welding

Repair welding of components, particularly of carbon steels that have been in sour service, must be approached with caution. However, successful repairs have been made for years in the sour gas and refining industries.

Prior to welding, hydrogen must be removed to avoid cracking. Removal may be accomplished with a combination of heat and time. Non-molecular hydrogen will diffuse out of steel given enough time. Unfortunately, molecular hydrogen trapped at manganese sulphide stringers and other sites will generally not diffuse unless extremely high temperatures are reached.

Degassing normally involves heating components to temperatures either just below or just above stress-relieving levels. At these levels hydrogen can diffuse rapidly from the metal.

After degassing, conventional welding procedures are employed. Welding is followed by stress relieving, either of the component as a whole, or locally, usually in a band around the item. Hardness tests, radiography, ultrasonics, and liquid penetrant are used to ensure the quality of the work.

For many years temper bead welding has been used to effect relatively small repairs in refineries and sour gas facilities. This method is based on a very controlled technique with limited heat input so that each bead tempers the one below it. The final bead is frequently ground or machined away to eliminate any untempered material.

If the process is carried out correctly, problems should not occur. However, cracking can happen if improper temper is obtained between beads (Ref. 42,117). Also, temper bead welding does not remove residual stresses and these can lead to cracking in sour environments (Ref. 175).

Testing of temper bead welds in sour environments indicated that cracking could occur between the fusion boundary and the weld metal in dissimilar metal welds (Ref. 81). In addition, if harder than anticipated heat-affected zones are encountered, Sulphide Stress Cracking could result even though the metals were not dissimilar. Consequently, for sour service, temper bead welding of large components (in which high residual stresses may occur) should be approached with caution.

12.5 Summary

Quality Assurance and/or Inspection of a component should involve a complete program covering its design, fabrication, installation, and operation. The program should incorporate vendor surveillance, on-stream inspection, and shutdown inspection. Non-Destructive Evaluation techniques should be used in conjunction with common sense, to identify and correct potential problems.

Table 12.1: Piping Corrosion Survey Sheet

Design Details	Isometric Sketch																																																																																																																																																
Plant No.: _____	Hardness: _____																																																																																																																																																
Line No.: _____	Corrosion Allowance: _____																																																																																																																																																
Eng. Spec.: _____																																																																																																																																																	
Drawing No.: _____																																																																																																																																																	
Line Description: _____																																																																																																																																																	
Line Size: _____																																																																																																																																																	
Material Spec.: _____																																																																																																																																																	
Design Pressure: _____																																																																																																																																																	
Design Temperature: _____																																																																																																																																																	
Max. Operating Pressure: _____																																																																																																																																																	
Max. Operating Temperature: _____																																																																																																																																																	
Hydrostatic Test Pressure: _____																																																																																																																																																	
Prior History: _____																																																																																																																																																	
<table border="1"> <thead> <tr> <th>Orig. Thk.</th> <th>Retire Thk.</th> <th>June 1983</th> <th>1984</th> <th>1985</th> <th>1986</th> <th>Cor. Rate</th> <th>Cor. Rate</th> <th>Cor. Rate</th> <th>Corr. Rdg.</th> <th>Rad. Repl.</th> <th>Cast Observations</th> </tr> </thead> <tbody> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td><td> </td></tr> </tbody> </table>		Orig. Thk.	Retire Thk.	June 1983	1984	1985	1986	Cor. Rate	Cor. Rate	Cor. Rate	Corr. Rdg.	Rad. Repl.	Cast Observations																																																																																																																																				
Orig. Thk.	Retire Thk.	June 1983	1984	1985	1986	Cor. Rate	Cor. Rate	Cor. Rate	Corr. Rdg.	Rad. Repl.	Cast Observations																																																																																																																																						

Date: _____ Inspector: _____ Equipment Used: _____
 Approved By: _____

13. SPECIFICATIONS USED FOR SOUR SERVICE

Because of the problems associated with oil and gas production in sour environments, material standards and recommended practices have been developed by the various industries to prevent premature failure. At first, individual companies developed standards based on their own experience but eventually concerned groups began to develop industry standards. The National Association of Corrosion Engineers, with a large petroleum-oriented membership, addressed the lack of standards, producing the most widely accepted document for materials for sour service (Ref. 1).

Sour service specifications started as a group of tentative recommendations to cover tubular goods, valves and welding. Although these recommendations had no formal standing, they were generally adopted by producers in Western Canada (the prime movers in establishing these specifications).

Valve problems continued to plague the industry so NACE Standard 1F166 was developed. This new specification proved to be less restrictive than the old, informal ones. Further studies resulted in NACE MR-01-75 "Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service" which replaced 1F166.

While this standard adequately controlled the materials for valves used in sour environments, it was being used also as a guideline for the selection of materials for other applications. Consequently, the standard was revised in 1978, and again in 1980, to cover all materials used in hydrogen sulphide environments.

13.1 NACE MR-01-75

This standard is called "Material Requirement - Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment". It includes materials used for equipment outlined for service under other standards such as API, ANSI, ASTM, ASME and CSA. However, it is intended solely for service where the main corrosion problem is Sulphide Stress Cracking. Excessive corrosion and Hydrogen Induced Cracking could make some of the material recommendations invalid. Nonetheless, its use does result in lowering the incidence of failure due to hydrogen sulphide environments.

13.2 NACE MR-01-76

This standard outlines the material requirements for "Metallic Materials for Sucker Rod Pumps for Hydrogen Sulfide Environments". This standard includes materials recommended for use in sucker rod pumps. However, it also cautions that an effective inhibitor program is essential in this service and, therefore, must be included in a comprehensive material selection program.

13.3 NACE TM-01-77

This document describes a method for "Testing of Metals for Resistance to

Sulfide Stress Cracking at Ambient Temperatures". Involving a slow strain rate test in a standard solution, this technique allows different laboratories to study materials under identical conditions. This test is used to evaluate materials for inclusion in NACE MR-01-75.

13.4 Proposed NACE Test Method for Elastomerics

The NACE has proposed a test method for Screening Elastomeric Materials for service in sour gas environments. The test will involve an accelerated aging procedure similar to ASTM D471, but the aspects of a sour environment under pressure has been added. The proposal is being voted on by the Committee members and, if approved, should be issued soon.

13.5 Step-Wise Cracking Test

NACE has proposed a test method for examining steels for resistance to Hydrogen Induced Cracking, particularly in the Step-Wise mode. The proposal is essentially the BP Test with a pH of 4.8 to 5.4. However, it will use fewer test pieces so that segregation areas may not be identified.

Because of the mild test environment, strong opposition to the proposal was voiced by the Canadian Sour Gas Industry and by the Heavy Water Industry. However, subsequent field pH tests at a Gulf Canada location suggest that the mild conditions might reflect those in some pipelines.

14. SUMMARY OF REPORT

The corrosion of steels in sour gas environments is a complex subject involving parameters such as pH, temperature, concentration of corroding species (including contaminants such as chlorides and carbon dioxide), and the presence of protective scales on the metal surface. Material failure is associated with a hydrogen cracking mechanism which is related to the strength of a steel: low strength alloys tend to blister, but high strength alloys tend to crack. Industry classifies these blistering and cracking defects as those that do not require the application of external stress (HIC), and those that do (SSC).

Although somewhat different aspects of failure are involved, both defects frequently occur together. Hydrogen Induced Cracking (HIC) may occur in the presence of an applied stress. In addition, stresses developing in an alloy as a result of hydrogen blistering (HIC), may reach a level high enough to create Sulphide Stress Cracking (SSC). Consequently, there can be considerable confusion in describing failures of sour service components.

The parameters which influence HIC and SSC may be classified as environmental or metallurgical. Since HIC and SSC frequently occur together, the effects of certain parameters are similar.

14.1 Environmental Parameters

Environmental parameters include pH, temperature, and concentration of corroding species and contaminants. Their effects are summarized as follows:

- (a) pH: corrosion rates tend to increase with decreasing pH.
- (b) Temperature: the critical range for corrosion and hydrogen damage under sour conditions appears to be 5-50°C. Raising or lowering the temperature out of that range decreases the damage.
- (c) Concentration of Hydrogen Sulphide: this is the one environmental parameter that produces some differences in its effect on the two forms of cracking. SSC susceptibility tends to be independent of the H₂S concentration as cracking has been encountered at 1 ppm levels. The rate of HIC, however, is strongly related to the amount of H₂S. The corrosion rate and subsequent hydrogen charging increase as the concentration of H₂S increases.
- (d) Contaminating Species: the presence of contaminants, such as sodium chloride and carbon dioxide, in the solution increases the corrosion rate and the susceptibility to both SSC and HIC; the effect of contaminants on HIC is more pronounced.
- (e) Protective Scales: the formation of iron sulphide scales on the surface of steels may reduce the rate of corrosion by preventing further dissolution of the steel. As a result, the lower corrosion rate reduces the amount of hydrogen available for charging, thereby decreasing the level of HIC.

14.2 Metallurgical Parameters

Both alloying elements and microstructure govern the response of a material to sour gas environment. Cracking tends to occur in untempered martensite or bainite which may form when alloying elements segregate during casting. High levels of manganese and phosphorus are known to segregate upon solidification and these alloys are often identified in and around sulphide-induced cracks. Furthermore, high concentrations of manganese and silicon in welds can produce dramatic increases in hardness with subsequent cracking. This is not surprising, considering the hardening tendencies of these alloying elements.

Hydrogen Induced Cracking initiates at elongated, non-metallic inclusions where the collection of diffusing hydrogen creates pressure sufficient to break metallic bonds or to fracture the metal. The hydrogen is generated by environmental corrosion of the steel surface. Tearing between hydrogen blisters on adjacent planes gives rise to a "Step-Wise" mode of HIC.

Certain alloying additions and efforts to lower the sulphur content greatly reduce susceptibility to HIC, particularly if the remaining non-metallic inclusions are preserved in a spheroidal shape - due to calcium treatment, or, to a lesser extent, to Rare Earth Metal additions.

The effects of metallurgical parameters may be summarized as:

- (a) Microstructure: SSC and HIC both tend to occur in banded structures where segregation of manganese and phosphorus occur. High levels of manganese can result in increased hardness and increased manganese sulphide inclusions. Rounding of the inclusions tends to reduce susceptibility to HIC, especially when coupled with lowering of the sulphur content to 0.001%. Heat treatment of banded structures (see (c) below) can improve their resistance to SSC.
- (b) Tensile Strength: increasing the tensile strength of a material increases its susceptibility to SSC. Use is made of the hardness versus tensile strength relationship to govern material quality and a maximum hardness, Rc 22, is specified as the limit for successful sulphide service. However, welds with hardnesses below this level have failed as a result of high stresses and/or of a severe environment.
- (c) Heat Treatment: Heat treatment must be geared to the structure of an alloy. Tempering of low transformation structures is necessary or cracking will occur. Some alloys possess structures that will be tempered only by heat treatments exceeding those normally employed. Quenched and tempered alloys appear to have the greatest resistance to SSC.
- (d) Deoxidation Practice: fully-killed steels experience HIC which initiates at manganese sulphide, alumina, and carbonitride particles. Semi-killed steels show greater resistance to HIC, due to a lower level of inclusions, and to the rounded shape of those inclusions that do exist.

- (e) Rolling Practice: controlled rolling tends to elongate non-metallic inclusions, thereby making the steels more susceptible to HIC.
- (f) Alloying Elements: a number of alloying elements may be added to aid in the formation of surface films to prevent corrosion. Copper with a solution pH above 5.0, appears to be particularly effective. At lower pH copper tends to increase the general corrosion rate.

The effect of nickel additions on the susceptibility of steels to corrosion is still a point of controversy. Currently, the volume of nickel added is kept below 1% to avoid cracking in sour service alloys.

14.3 Corrosion

Corrosion of steels in sour gas environments can be classified according to the response of a material to hydrogen sulphide.

14.3.1 Carbon and Low Alloys

Corrosion of carbon and low alloy steels in sour gas environments occurs in the presence of moisture. It produces a number of defects:

- (a) Pitting: pitting tends to form below liquid level lines. The pits are large and randomly oriented.
- (b) Erosion/Corrosion: Removal of the protective sulphide layers results in rapid corrosion of the underlying steel. Corrosion rates may reach 25 mm/year. Velocities must be controlled to prevent scale removal.
- (c) Sulphide Stress Cracking: SSC is characterized by a single relatively straight crack. It is associated usually with welds, either in the weld deposit or in the heat affected zone at hard spots. Failure is generally sudden due to the brittle nature of the defect.
- (d) Hydrogen Induced Cracking: HIC is characterized by the formation of blisters which may link in a "Step-Wise" mode. The blisters initiate at non-metallic inclusions.

14.3.2 Austenitic Alloys

Corrosion of austenitic alloys is confined generally to pitting or cracking of cold worked structures. The cracking usually occurs in the presence of sulphide solutions contaminated with chlorides. Sensitization of austenitic alloys by excessive heat treating or poor post weld heat treating can result in intergranular corrosion; sulphur-oxy-acids form if a system is exposed to air. Neutralizing the streams before the equipment is opened corrects the situation.

14.3.3 All Steels

Cold working of both carbon steels and austenitic alloys can lead to increased

susceptibility to cracking; this process raises the hardness of the material above the maximum recommended by NACE for hydrogen sulphide service.

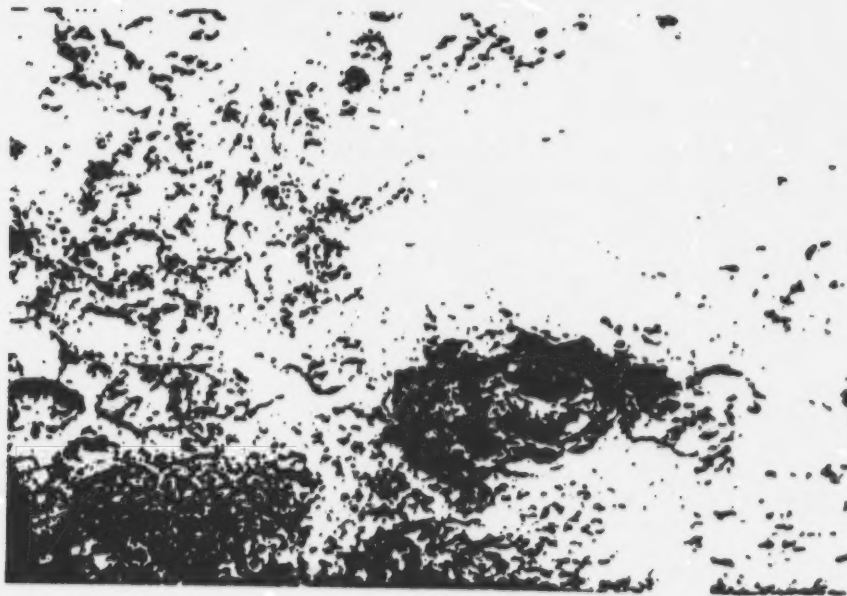
14.4 Corrosion Inhibitors

Corrosion inhibitors, effective in hydrocarbon bearing systems, may be totally unacceptable in Heavy Water Systems as these systems do not contain oil.

In addition, inhibitors may enhance hydrogen entry into the steel or destroy protective sulphide scales.

14.5 Quality Assurance

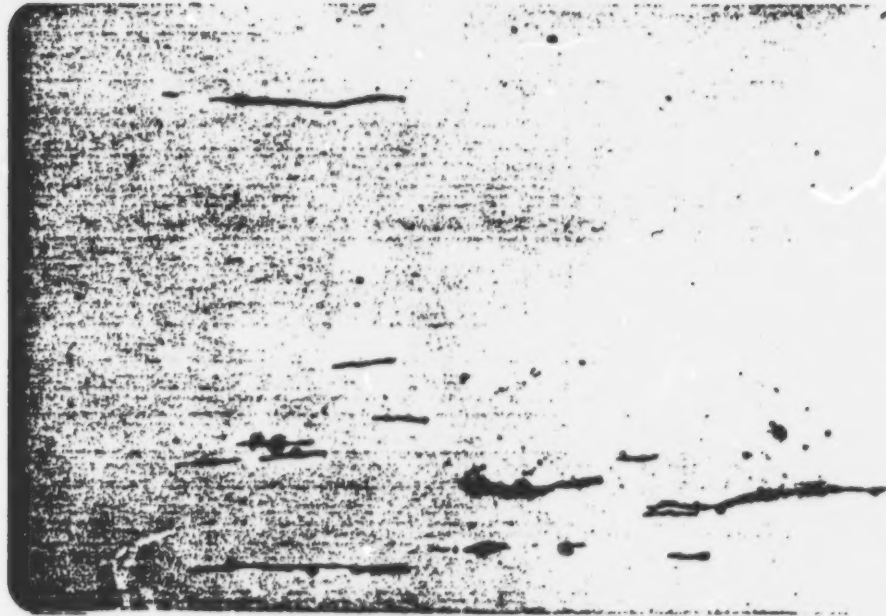
An effective and strongly enforced quality assurance program is seen as the most basic factor in controlling both SSC and HIC. This program, extending to both manufacturing and operating aspects, should be governed by written policies and procedures with deviation permitted only if field or laboratory experiments demonstrate clearly that damage is unlikely.



Photograph 1 - Typical sulphide induced pit with the oyster shell marking characteristic of wet hydrogen sulphide corrosion on carbon steel.



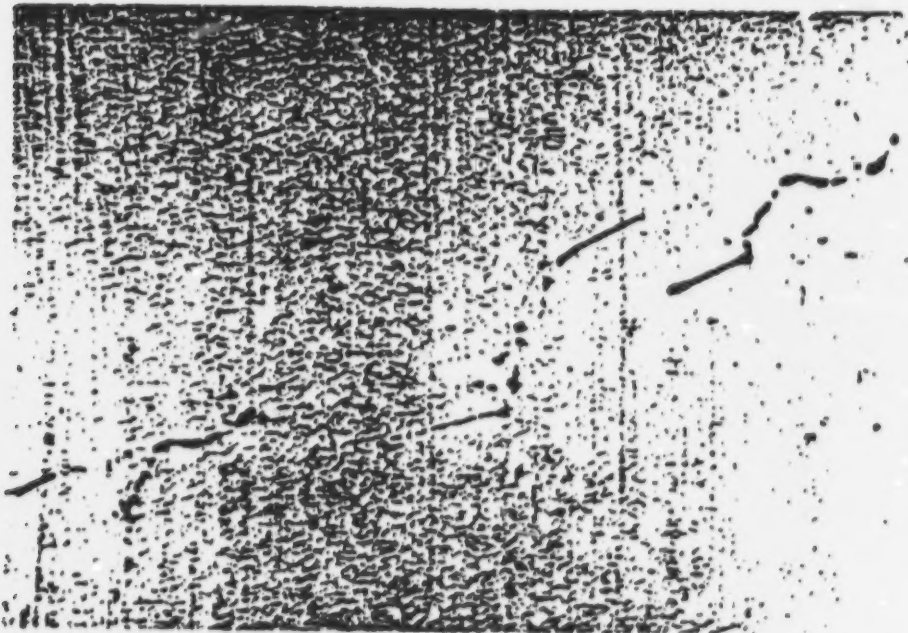
Photograph 2 - Elongated manganese sulphide stringers in Control Rolled ASME SA 516 Grade 70 carbon steel plate. (Magnification 200X)



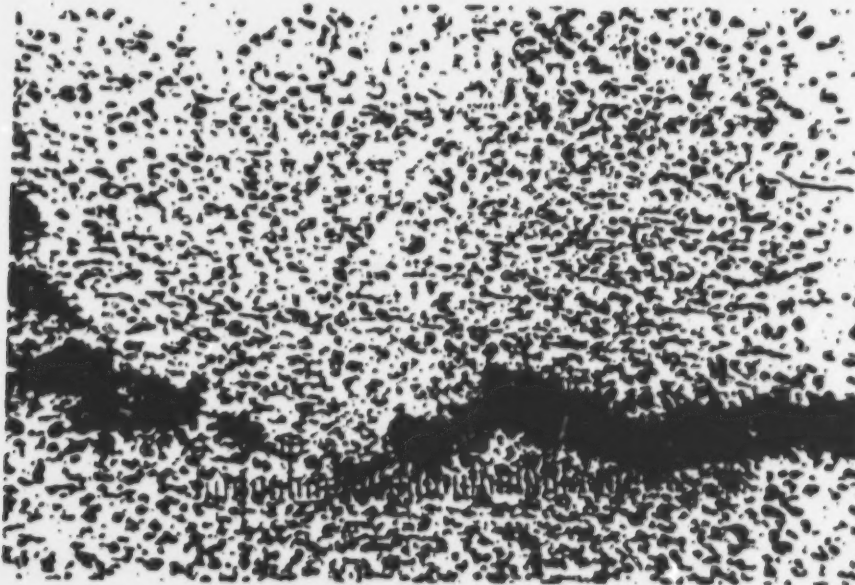
Photograph 3 - Elongated manganese sulphide stringers in Control Rolled ASME SA 516 Grade 70 carbon steel plate. Hydrogen has collected at some stringers and has caused the starting of blistering. (Magnification 200X)



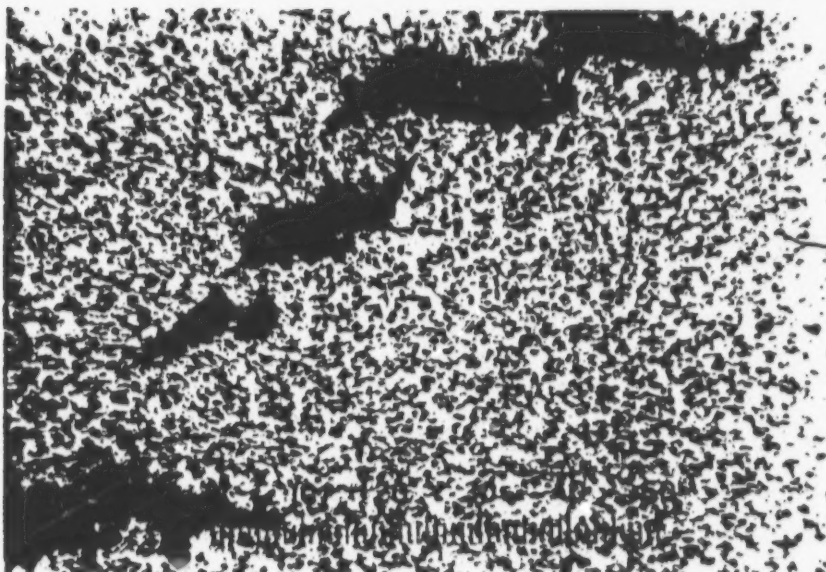
Photograph 4 - Elongated manganese sulphide stringers in Control Rolled ASME SA 516 Grade 70 carbon steel plate. Hydrogen blisters have progressed to the enlarging state. (Magnification 100X)



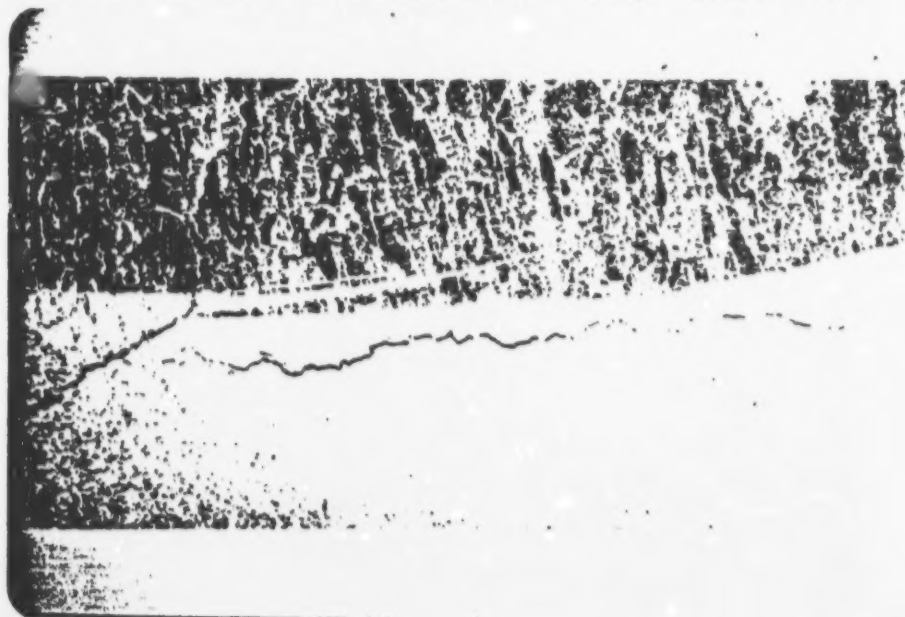
Photograph 5 - Elongated manganese sulphide stringers in ASME SA 516 Grade 70 carbon steel plate. Control Rolling may have been employed to a limited extent. These stringers have formed in a "Step-Wise" mode suggesting that inclusions may be partially responsible for this crack mode in some steels. (Magnification 200X)



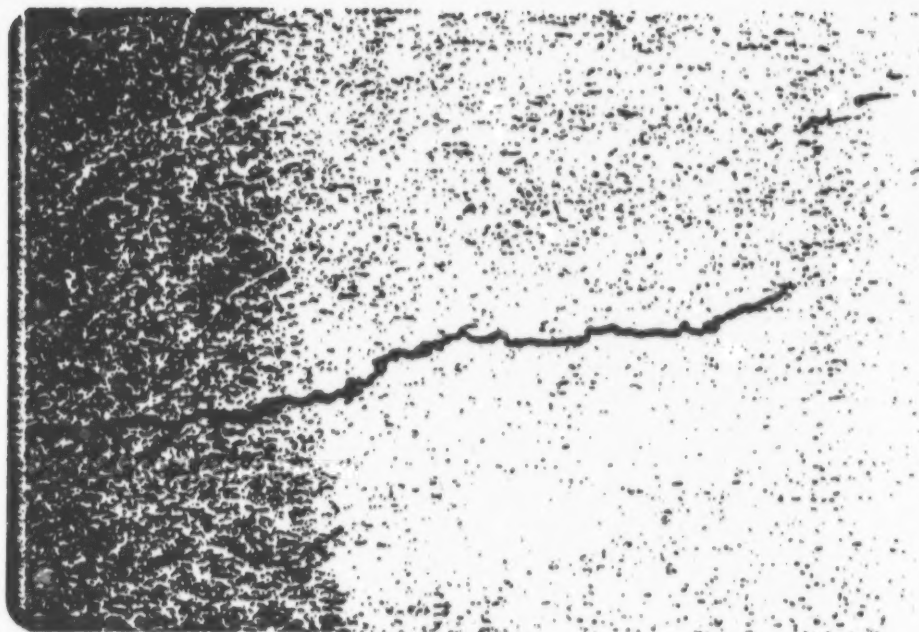
Photograph 6 - "Step-Wise" cracks in ASTM SA 516 Grade 70 plate. Tearing has occurred between defects in different planes. (Magnification 50X)



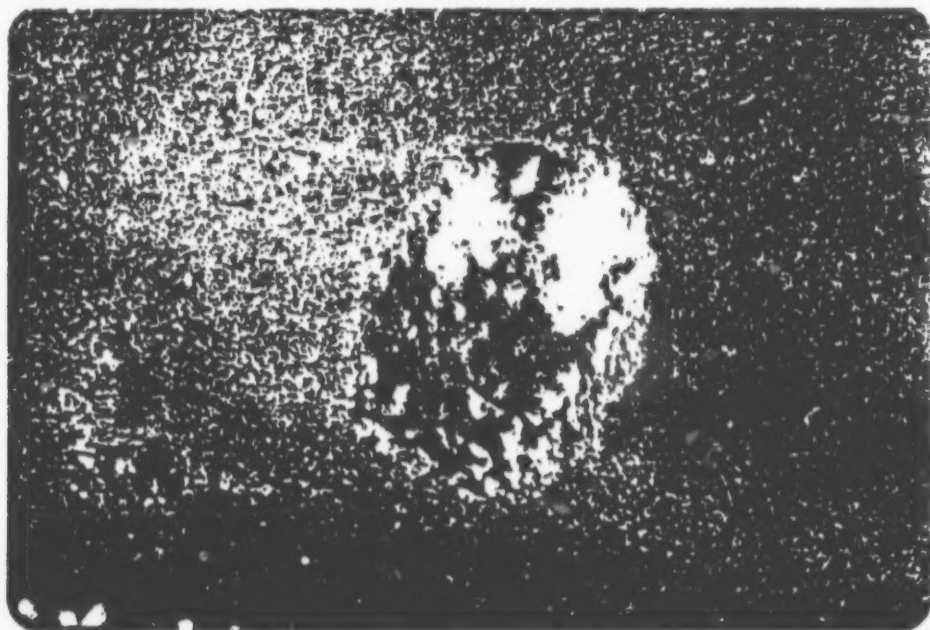
Photograph 7 - "Step-Wise" cracks in ASME SA 516 Grade 70 carbon steel plate. Tearing between blisters in different planes is evident by the thin sections joining larger defects. In addition, a crack can be seen extending from the end of a blister in the direction of another defect. (Magnification 50X)



Photograph 8 - Sulphide Stress Crack in the heat-affected zone of a weld after Bieffer, Reference 165. The crack shows some branching tendencies (in keeping with low strength material). (Magnification 100X)



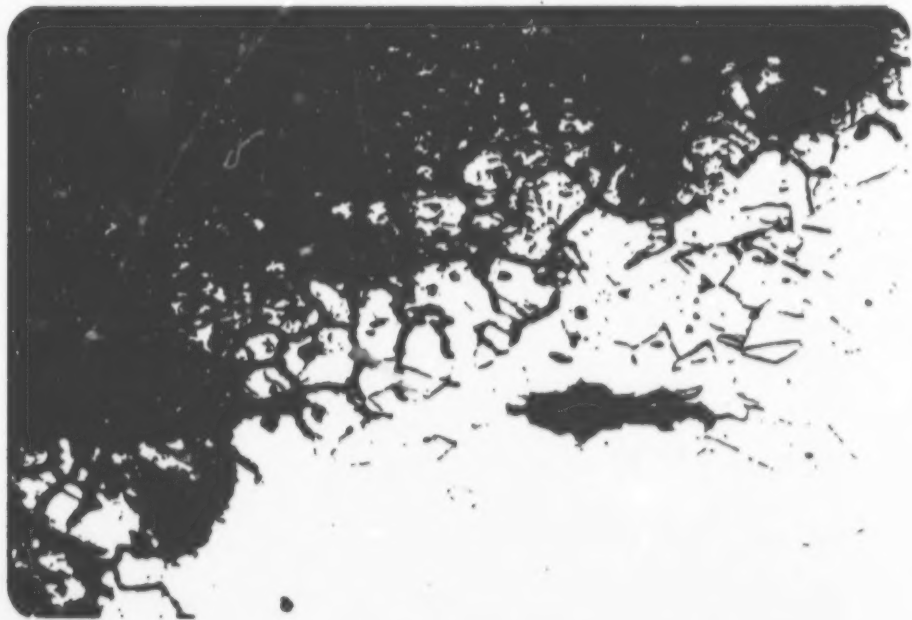
Photograph 9 - Sulphide Stress Crack in weld metal after Biefer and Fichera, Reference 164. The crack, typical of SSC, is relatively straight with only slight branching tendencies. (Magnification 100X)



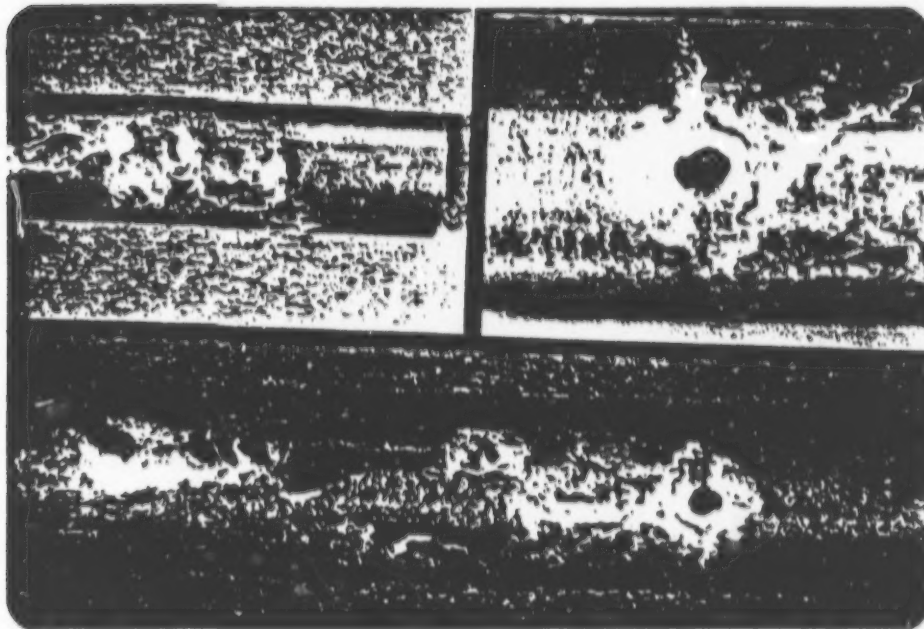
Photograph 10 - Typical pit found in type 304 stainless steel in wet hydrogen sulphide environments.



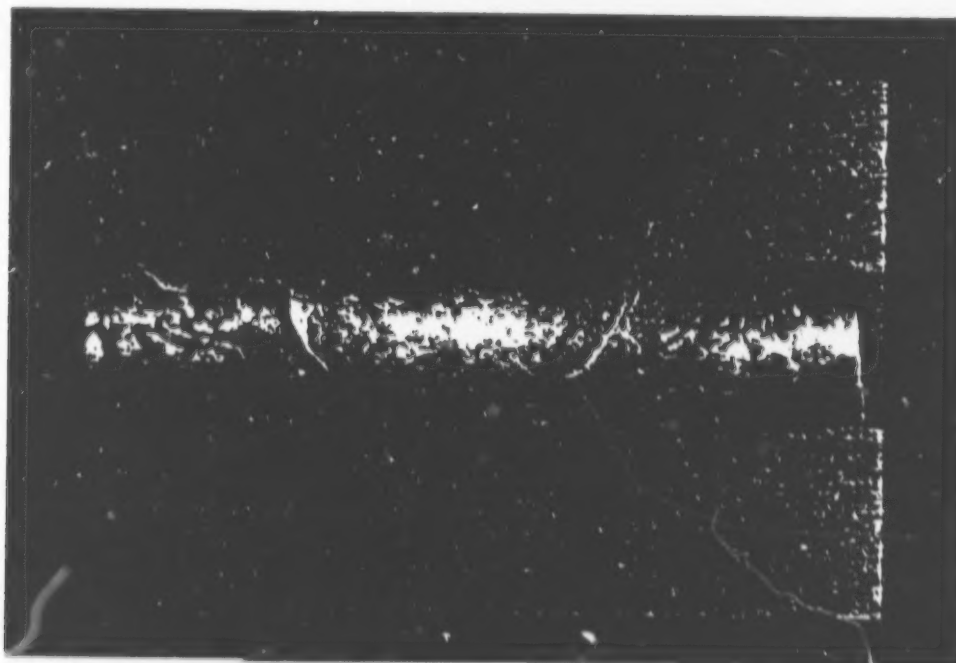
Photograph 11 - Transgranular cracking produced by hydrogen sulphide solutions on cold worked, austenitic stainless steels. (Magnification 100X)



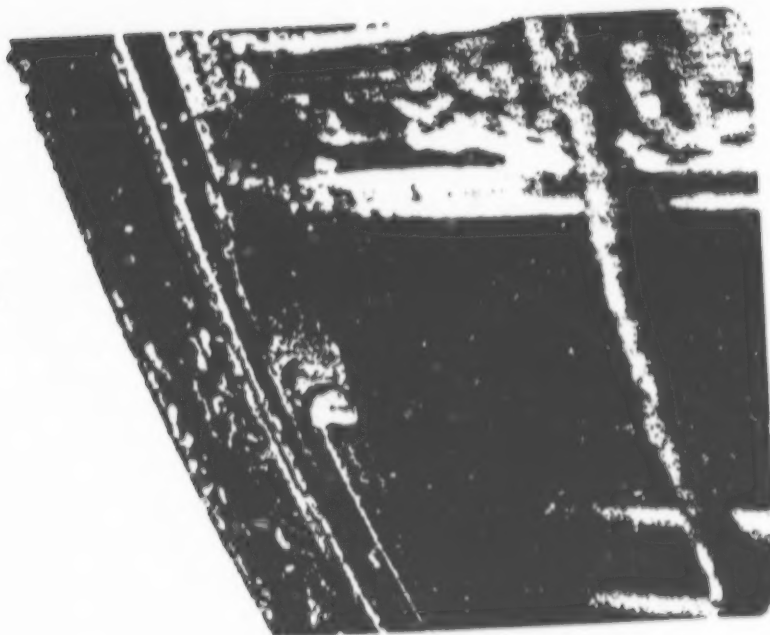
Photograph 12 - Intergranular corrosion of sensitized structure due to sulphur-oxy-acid. (Magnification 100X)



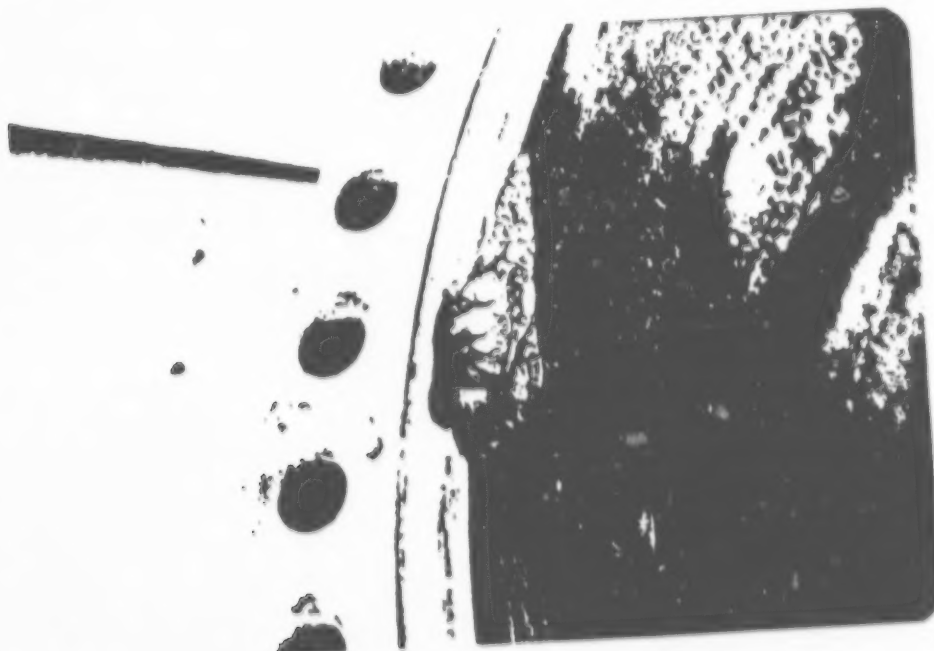
Photograph 13 - Deposits on austenitic stainless steels produce both pits and various patterns, outlining the successive edges of the deposit. (Type 304 stainless steel).



Photograph 14 - Although molybdenum-containing alloys are resistant to pitting and crevice corrosion, deposits can produce corrosion patterns on Type 316 stainless steels, as a result of differential aeration factors, in hydrogen sulphide environments.



Photograph 15 - Erosion/corrosion of the back of the tube sheet of a two-pass heat exchanger from a Heavy Water Plant. Erosion was caused by turbulence due to by-passing of the longitudinal baffle.



Photograph 16 - Erosion/Corrosion of the flange of a two-pass heat exchanger shell, due to by-passing of the horizontal baffles.



Photograph 17 - Erosion/Corrosion of the shell of a two-pass heat exchanger, due to by-passing of the horizontal baffles. The defects were extremely large, measuring up to 15 cm in diameter. Galvanic contact between the stainless steel baffles on the carbon steel shell may have contributed to the corrosion.



Photograph 18 - Two-phase flow can result in a typical erosion pattern, forming a groove in the material generally following the liquid/gas interface.

REFERENCES

See Appendix B for References.

APPENDIX A

Comments on References

A. COMMENTS ON REFERENCES

Papers on hydrogen sulphide corrosion tended to follow a cyclical pattern (from 1940 to 1970). First, case histories outlining failures, particularly in the sour gas and refining industries, would be published. These would be followed by research and laboratory studies determining the effects of such aspects as alloying elements, microstructure and solution composition on resistance to sulphide stress cracking. In time, new case histories would appear, followed by more research studies.

This cyclical pattern was, in all probability, the result of the "new engineer" syndrome. Experienced personnel who dealt with failures and devised methods to combat them were promoted, left the company, or were no longer involved in material problems. They would be replaced by less experienced people who, failing to review previous history, would go through the same learning patterns as their predecessors. Consequently, materials that might not be suited to the service would be used, with resultant failures. This was naturally followed by the publication of case histories (of failures) which triggered more research-oriented work.

This was vividly illustrated at a conference a number of years ago when representatives of the company that first developed sour service specification bolting, pleaded for assistance to help solve cracking problems in the products they were buying. Old records had been destroyed in an austerity move and no one remembered that the bolt development had been undertaken by their personnel.

The pattern was broken with the publication, in 1976, of Moore and Warga's work (Ref. 7) concerning the Step-Wise Cracking of line-pipe steel. Since then, the development and research work has continued at a frantic pace, fuelled by steel companies hoping to sell their products to the rapidly growing petroleum and natural gas markets. More recently, shrinking world economies have produced aggressive marketing, trying to prove that "our products are better than our competitors".

Japanese companies with their modern mills and highly qualified research engineers have published extensively, producing some extremely valuable work. Their papers tend to be very detailed but also somewhat repetitious as varied groups of authors, from the same company, may publish in a number of journals over a short period. Each article will repeat previously published material, adding only a small amount of new information.

These Japanese scientists and engineers have advanced a number of new concepts with respect to Hydrogen Induced Cracking. In establishing most of the currently accepted criteria relating to HIC, they have revived some concepts previously developed in the United States.

European authors entered the international scene about the same time as the Japanese, but with few sour gas fields, they have not been as prolific.

North American companies that originally identified the problems related to sour gas and were responsible for the vast majority of early papers, have responded to the "challenge" producing new discoveries of their own. Their main difficulty is producing "clean" steels in old mills.

Most of the early publications on Hydrogen Blistering and Sulphide Stress Cracking are found in U.S. journals. The large American oil companies were actively involved in developing oil and gas fields around the world. The National Association of Corrosion Engineers with its offices in the heart of the U.S. oil country has been a leader in the development of standards and specifications for sour service equipment. As this organization grew in international membership and status, its conferences and technical symposia attracted authors on a world-wide basis. In addition, its documents have been accepted internationally as the general guidelines to be used in construction for sour conditions. Therefore, most of the publications concerning sour environments may be found in the journals, technical symposia proceedings and conference proceedings of this organization.

The following literature survey basically involves articles published in the 1970 to 1983 era. Certain classic papers from earlier years have been included to illustrate the identification of the various problems, the solutions proposed and the research work generated. Some of the theories of damage have been modified over the years, but the practical approach to identifying, describing and solving problems make these papers as relevant as when they were written. Some of the modern works that have concentrated on very narrow, and often minor, aspects of hydrogen sulphide damage will not fare as well.

A.1 Classification of Papers

Papers reviewed in this study may be classified in four groups, namely -

- (a) Case histories of failures, prepared by plant personnel, consultants, or research facilities associated with the plant, or engaged by the plant to determine cause of failure and remedial action.
- (b) Publications by research facilities, including universities, government agencies, and independent test laboratories.
- (c) Information provided by metal manufacturers or fabricators and their associated research facilities. This may also include contract research to the establishments in category (b).
- (d) Literature review papers.

A.1.1 Case Histories

The case history papers are the most important. They represent problems that have occurred in industry under various operating conditions. These conditions, with the resultant cracks and blisters, are described in detail augmented by photographs to illustrate the problems. Consequently the reader is able to

assess what might happen should he attempt to use the same materials under similar conditions.

Of equal value are the solutions that have been used to cure the problems. These solutions are based on practical aspects considering what can be done in the field. Obviously, it is of little use to expect field personnel to follow a repair procedure involving strict laboratory conditions.

Research projects, based upon equipment failure, can be very informative. Their value in solving problems depends on the approach, the test conditions, and the actual tests.

Many projects, establishing that cracking takes place in segregation bands, have identified various alloying elements that contribute to the problem. In efforts to overcome one problem by using fully-killed steels with high alloy contents to yield good impact properties, another one, in the form of hydrogen blistering at non-metallic inclusions, has been created. It is interesting to note that older papers referred to the use of fully-killed fine grained steels to overcome cracking and blistering while newer ones are advocating the use of semi-killed material to control non-metallic inclusions and their shape.

Neither recommendation would be particularly useful if the steels possessed structures prone to cracking and segregation zones that could not be modified by rolling and/or heating.

Heat treatment also plays an important role in the success of an alloy and research projects have revealed that commercial heat treating practice may be insufficient to produce crack resistant structures. Consequently, the prior heat treat history of an alloy must be known before any subsequent treatments are performed - a situation all too frequently overlooked by many manufacturers.

A great deal of laboratory-generated data tends to have poor correlation with field data due, in part, to the complete immersion of samples in the solutions so that hydrogen charging occurs from all sides, rather than from one side as would be the case in a pipeline or vessel.

Full-size pipe test experiments, as carried out by the Japanese with charging from only one side, or the coating of all but one side of coupons, have helped to simulate field conditions and better correlation between laboratory and field results has been obtained. However, some laboratory experiments appear to be designed to produce predetermined results. This is demonstrated by the use of laboratory-produced heats which are made under controlled conditions that cannot be repeated on a commercial basis. Consequently, while the results are very interesting they really have little relevance to what might be expected of commercial alloys in the field.

The same is true of welded samples. Laboratory-produced welds may show great resistance to cracking but these high quality samples may not be representative of the products that the welders can give under field conditions. Therefore, testing of samples as they will be used in the field should be advocated.

A trend also was noted with some company-produced papers. They tend to be a restatement of work that had been done by others many years earlier. Old concepts that have been discarded are put forward as new ideas.

A.1.2 Research Facilities

Research facilities have generated work that has been beneficial to the industry as a whole. Work on preconditioning of carbon steels to reduce corrosion levels through the formation of a protective scale, investigations of pipeline failures, testing of material as an independent institution, and assistance in developing a standard test technique, are cases in point.

These facilities tend to use high strength steels in experiments to promote failure in a short time and then relate the results to lower strength alloys through mathematical modelling. While this is perfectly acceptable in many instances, it would seem prudent to test the actual materials that have failed. (This has been done in many cases but not all.)

In addition, it was noted that some research-associated papers purport to study the effects of certain alloying elements while totalling ignoring the effects of other elements in the steel. The effects of combinations of elements cannot be ignored; this has been aptly demonstrated for many years. European authors, and to a lesser extent some North American authors, tend to be guilty of these oversights.

A.1.3 Alloy Manufacturers and Fabricators

Alloys are continually being submitted to the NACE for approval to MR-01-75. Many of these alloys require very complex heat treatments to produce structures resistant to SSC or HIC. Overaging, double overaging, or multiple quench and temper treatments are employed regularly. One NACE committee member was heard to exclaim that the heat treatments are becoming so complicated that soon success will depend upon how the heat treater holds his mouth. While this is obviously an exaggeration, the complicated heat treatments do present areas of potential problems and one would be advised to use the alloys with the least complicated procedures.

Many large, reputable companies have produced papers on their products intended for hydrogen sulphide service. These should form a valuable addition to any library. This is particularly true of high alloy materials and microalloyed, ultraclean carbon steels.

A.1.4 Literature Reviews

Literature reviews have been conducted by authors in many countries. Most cover their subjects well stating both the pros and cons of dissenting information. However, a few authors, particularly some European ones, appear to start with a preconceived idea and then cite only those authors who support this point of view. In addition, many of the European literature reviews appear to be quite dated as their information ceases 18 months to 2 years prior to the publication of their reviews. Perhaps this is due to difficulty in obtaining up-to-date information from North America and Japan.

A.2 Papers on Alloying Elements

Controversy might be considered as a central theme running through this material. Perhaps the nickel content limits applied by the NACE exemplify this controversy.

Many older papers report severe Sulphide Stress Cracking in alloys containing significant amounts of nickel. Newer papers outline experimental results showing that nickel has no effect upon the cracking susceptibility of steels. Some of these works apparently ignore the beneficial effect of other alloying elements. Others employ laboratory heats and laboratory produced welds - conditions that cannot be duplicated in the field. Still others conclude that nickel has no effect when their test results suggest otherwise. (Some problems in translation from the original language of publication might account for this.)

Field experience has indicated that alloys containing nickel suffer reduced resistance to SSC. This was demonstrated in the heavy water industry when a repair weld of a carbon steel component accidentally suffered nickel pick-up and cracked quickly in service. Consequently, the restriction on nickel to less than 1% should be maintained until more information has been generated through controlled experiments.

Copper has also been a centre of controversy with many Japanese authors claiming it reduced HIC susceptibility with experimental results to prove it.

Environmental test conditions were not fully detailed initially but a great deal of subsequent testing revealed that while copper was beneficial under the relatively mild conditions of the BP Test (pH about 5.0) it, in fact, promoted excessive corrosion in test environments simulating heavy water plant conditions (pH 3.0-3.5). The excess hydrogen generated helped to promote HIC.

One must carefully examine an alloy and use it in test conditions closely approximating those of the plant environment. In addition, references must be carefully analyzed to assess the severity of the test environment. There is a tendency to make the test solutions less aggressive so that many alloys will pass. For instance, the NACE T-1F-20 committee on HIC testing adopted a proposal to use the milder BP Type solution, rather than the originally proposed NACE solution (more aggressive) over the objections of many consumers (the Sour Gas Industry and the Heavy Water Industry to name two). Japanese manufacturers, on the other hand, have demonstrated the necessary restraints that must be placed on steels to meet the more aggressive solutions - namely, low sulphur content and inclusion shape control.

A.3 Papers on Welding

Welding has also attracted considerable attention as SSC tends to be associated with it. Cracking takes place in both welds and heat affected zones in hard

spots with microstructures prone to cracking. The refining industry has known for years that Rc 22 is not a practical hardness limit for certain welds. Alloying elements such as manganese can produce hard structures, particularly in submerged arc welds. Failures in pipelines with hardness at, or below, Rc 22 may be exhibiting this tendency.

Heavy water plant practice to limit hardness to Rc 22 or even lower to allow for some cold working is commendable. However, heat treatments employed may not produce the desired structures so control over welding consumables is also exercised to prevent the formation of susceptible areas.

A.4 Papers on Damage Considerations

Although the theories of SSC and HIC are many and varied, they contain one central theme, that of a hydrogen cracking mechanism. All papers referenced, concur on this subject. They also agree that the hydrogen is generated on the surface of the alloy by corrosion caused by aqueous hydrogen sulphide. Removal of the hydrogen sulphide or the moisture will stop the attack and the cracking.

Whether or not the cracking is the result of hydrogen pressure or decohesion of the inclusion/alloy matrix, is irrelevant if levels of hydrogen are kept low enough to prevent cracking. Monitoring the levels can be done effectively with probes.

Damage induced in materials may manifest itself in different ways. SSC will result in a sudden brittle rupture. Cracks may be quite long and damage may not be detected prior to failure. HIC, on the other hand, will probably result in weepage of components long before any cracks become large enough to result in brittle failure. HIC damage can probably be detected through special monitoring techniques. Consequently alloy selection, welding specifications, and other fabricating techniques should be made with a view to ensuring that HIC is the mode of damage and not SSC.

Unfortunately, SSC can also initiate at HIC damage, either due to the stresses generated by the hydrogen or to a combination of these stresses and operating-induced stresses. These cracks will tend to propagate in the through-wall direction. The cracks will continue until the high stresses are relieved and then they stop. If hydrogen stresses are able to build up again, or if the operating pressures are sufficient, a new crack may appear or the old one may propagate again. Under these circumstances, small leaks generally occur, but extremely large defects could be created depending on the severity of the service environment.

Defects can be successfully repaired by welding, providing degassing is carried out first. Degassing may involve a myriad of heat levels depending upon which industry is involved. Heat levels ranging from as low as 93°C and as high as 598°C have been used but that most frequently encountered is 149°C to 315°C with a minimum holding time of three hours. It must be emphasized that repairs made at low degassing temperatures usually involve equipment that has been open to the atmosphere for many days prior to the work.

A.5 Abstracts

Articles relevant to this report have been abstracted in the reference section. The abstracts are designed to highlight the important parts of a paper as may be applicable to the heavy water and sour gas industries. The contribution of certain papers to this report has been noted.

APPENDIX B

References

ABSTRACTED REFERENCES

1. NACE-MR-01-75 "Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment"

Approved 1975, Revised 1978, 1979, 1980 - Currently under review for another revision.

2. Y. Nakai, O. Haida, T. Emi, K. Hirose, H. Motate, 'Development of Line Pipe Steels Resistant to HIC in Wet Hydrogen Sulphide Environment' - Presented at Middle East NACE Corrosion Conference, Bahrain, April 15 to 17, 1979

Hydrogen Induced Cracking concentrated in the segregation zones of ingots or along the centreline of continuous cast slabs. HIC could be decreased, but not eliminated, by reducing the sulphur to 0.001 %. The addition of alloying elements such as copper, reduced the rate of hydrogen permeation and subsequent cracking, but only under conditions of moderate pH. Heat treating to make the structure more homogeneous decreased the susceptibility to HIC but shape control, impractical in commercial heats, was more effective. However, rare earth additions and/or calcium in an atomic ratio greater than 1.5 with sulphur were most effective in producing a steel highly resistant to HIC.

This is a very informative paper.

3. Jack L. Battle, T.V. Miller and Martin E. True of Exxon Company, 'Resistance of Commercially Available High Strength Tubular Goods to Sulfide Stress Cracking', "Materials Performance", Volume 14, No. 6, June, 1975

The performance of API C-75, N-80, modified N-80 and higher strength materials in hydrogen sulphide environment was studied. It was found that the upper yield strength limit for resistance to H₂S for commercial products was 550 MPa (80,000 psi). With the exception of the 620 MPa (90,000 psi) yield strength AISI 4130, higher strength steels designed for H₂S service did not perform well.

Points Noted:

- (1) Steels from different manufacturers varied in quality.
 - (2) The thicker the steel the poorer the performance.
 - (3) As pH increased higher tensile strength steels could be used.
 - (4) Quench-and-tempered materials performed well.
4. 'Corrosion in Hot, Deep, Sour Gas Condensate Wells', "Materials Performance" Volume 14, June, 1975, No. 6 - Report of Committee T-1 Panel Discussion

SSCC increases with partial pressure of H₂S with 0.001 atmospheres identified as the critical level.

In lead-containing, free machining steel, SSCC has occurred at hardnesses below Rc22.

Quench-and-tempered structures are the best performers.

SSOC produces cracks with extensive branching in high strength material and less branching in low-strength materials.

5. Harvey J. Henricks, 'Corrosion Monitoring in the East Cross-Field D-1 Gas Gathering System', "Materials Performance", Volume 14, No.14, December, 1975
-

A Corrosion Monitoring Program is outlined. No problems were encountered as long as the well was inhibited with an oil-soluble, water-dispersable amine inhibitor. Brittle fracture was encountered on equipment such as subsurface safety valves, hydrogen probe elements, thermowells and coupon retrievers. The program indicated low corrosion activity.

This paper is quite general.

6. Donald S. Burns, 'Laboratory Test for Evaluating Alloys for H₂S Service' "Materials Performance", Volume 15, No. 1, January, 1976
-

Accelerated tensile stress tests of materials suitable for petroleum production under hydrogen sulphide conditions are described. Welded carbon steel coupons in the 137 to 200 BHN range blistered and failed at less than 43% of the designated yield strength, largely in unwelded zones. Tubular goods tended to fail due to interrelated factors: wall thickness, stress, time, and method of hydrogen charging.

Problems Cited:

- (1) Accelerated laboratory tests do not always agree with field data.
- (2) Accelerated lab tests generating data on conventional acceptable oil field materials are not readily available.
- (3) There is no universally accepted test method.
- (4) Hollow samples charged from one side react differently to solid samples.

Results:

- (1) Low strength steels blistered.
- (2) High strength steels cracked.
- (3) Welds and HAZs were not as susceptible to the test environment as the base metal.
- (4) Controlled welding can raise the test limit stress to 90% from 43% of the yield for failure in carbon steels.

An excellent paper, this article addressed the difference between field and laboratory generated data.

7. E.M. Moore and J.J. Warga, 'Factors Influencing the Hydrogen Cracking Sensitivity of Pipeline Steels', "Materials Performance", Volume 15, No. 6, June, 1976
-

This paper was the beginning of considerable HIC-related research.

Case History:

In 1974, three service ruptures occurred in a spirally welded, API 5LX - Grade 42 sour gas transmission pipeline, four to seven weeks after commissioning. Extensive blistering and cracking were found. All failures were due to step-wise cracking associated with elongated manganese sulphide inclusions. Blistering was often, but not always, evident in the cracked areas. The failures were always located near the spiral weld but were never identified with weld defects. Blistering and incipient cracking occurred randomly on the bottom and sides of the affected sections of the pipeline. No defects were found in the top quadrant of these pipes.

No correlation was found between hydrogen cracking sensitivity and mechanical properties of the steel.

No correlation was found between weld or heat affected zone structures and cracking. Indeed, no cracking was found in these areas.

It was found that the deoxidation practice greatly affected the cracking tendency. Steel making practice using aluminum for deoxidation and employing controlled rolling result in the formation of Type II or long, thin MnS inclusions. This type of inclusion promotes blistering and/or cracking.

8. J.B. Greer, 'Results on Interlaboratory Sulfide Stress Cracking Using the NACE T-1F-9 Proposed Test Method', "Materials Performance", Volume 16, No. 9 September, 1977
-

The results of testing by eighteen companies using the T-1F-9 Proposed Test Method are summarized. It is concluded that the Proposed Test Method for constant load smooth tension specimens is sufficiently reproducible to provide an NACE standard.

The sulphide stress corrosion cracking data were determined to be logarithmically related to time $\sigma = \sigma_0 - \beta \log t$ where

σ is stress

σ_0 and β are material constants

t is time

Microcracking and blistering in low strength steels occurred sufficiently frequently to render the logarithmic relationship invalid. Failure tended to be from blistering and microcracking rather than from SSCC.

9. Ronald B. Diegle and R.S. Treseder, 'Resistance of Ductile Iron to Sulfide Stress Cracking', "Materials Performance", Volume 17, No. 6, June, 1978
-

Ductile Iron (A-395), tested using the NACE-T-1F-9 test procedure, was found to have a test limit stress of 95% of yield, considerably higher than for carbon

steels. The difference was attributed to the cast structure and to the low sulphur content.

10. D.P. Dautovich and M.G. Hay, 'Iron Sulfide Coatings to Reduce Hydrogen Damage in H₂S Environments' "Materials Performance", Volume 17, No. 8, August, 1978
-

Preconditioning used to produce a stable sulphide layer on carbon steel surfaces prior to operation of heavy water plant equipment prevented or reduced hydrogen charging and, hence, subsequent blister cracking.

11. Eddie C. French, 'Corrosion and Hydrogen Blistering in Sour Systems', "Materials Performance", Volume 17, No. 3, March, 1978
-

The effects of cyanide, polysulphide, and inhibitors on the corrosion rate and hydrogen blistering of fluid catalytic gas recovery was determined using autoclaves and continuous monitoring of the corrosion and hydrogen permeation rates. Polysulphide reduced corrosion by converting cyanide to thiocyanate and shifting the corrosion potential out of the hydrogen generation region. However, large amounts of polysulphide can increase the corrosion rate. A proprietary water soluble inhibitor also proved effective in reducing hydrogen blistering.

This is a good general paper exploring corrosion in refinery systems.

12. B.R.D. Gerus and J.N. Cassin, 'Corrosion in the Burnt Timber Wet Sour Gas Gathering System', "Materials Performance", Volume 17, No. 3, March, 1978
-

This article describes four years' operating life of a natural gas pipeline. Eight leaks developed over the period, all due to pitting caused by water and accumulated sludge. Inhibition was employed with variable success, possibly due to continuing changes in inhibitor feed rates and to changes in inhibitor.

13. B.E. Wilde and J.M. Doyle, 'A Comparison Between Threshold Stress and "Crack Initiation" Stress Intensity for Sulfide Stress Corrosion Cracking', "Corrosion", Volume 35, No. 6, June, 1979
-

The authors describe a method of accelerated testing. Their observations of trenching underneath sulphide scales are of prime importance. The trenches were observed to grow perpendicular to the direction of applied stress. This may be indicative of a strain assisted anodic dissolution process, not normally considered to be operative during SSCC.

14. B.E. Wilde, C.D. Kim and J.C. Turn Jr., 'The Influence of Noble Metal Additions on the Sulfide Corrosion Performance of AISI 4130 Steel', "Corrosion", Volume 38, No. 10, October, 1982
-

Additions of Cu, Ag, palladium, platinum and nickel were made to a 690 MPa yield strength AISI 4130 steel. The results showed that copper, silver and nickel additions of 0, 0.05, 0.1, 0.5 and 1.0 weight % had no effect.

Palladium and platinum in concentrations in excess of 0.5 wt. percent rendered the steels immune to SSCC and HIC.

15. A.R. Troiano and R.F. Hehemann, 'Hydrogen Sulfide Stress Corrosion Cracking in Materials for Geothermal Power', "Materials Performance", Volume 18, No. 1, January, 1979
-

Tests on a wide range of structural steels and high alloy were carried out in H₂S saturated, chloride solutions. High temperatures reduced susceptibility to cracking. Increased pH resulted in decreased corrosion.

16. J.P. Hirth and H.H. Johnson, 'Hydrogen Problems in Energy Related Technology', "Corrosion", Volume 32, No. 1, January, 1976
-

A survey was made of hydrogen degradation problems in energy related systems. Nine phenomenological classifications of damage are present. This is a good paper classifying types of damage. Some information is dated but this is still a very valuable reference.

17. J.H. Payer, A.G. Preban and H.P. Leckie, 'Hydrogen - Stress Cracking of Low Carbon Martensitic Steel', "Corrosion", Volume 32, No. 2, February, 1976
-

Low carbon martensitic steel was found to be less susceptible to hydrogen stress cracking than either cold-rolled, AISI-1055 steel or quenched and tempered AISI-1074 steel at the same strength levels. Susceptibility to hydrogen stress cracking increased with increasing ultimate tensile strength. Cold working or tempering appeared to affect the susceptibility. The threshold stress below which HIC does not occur, decreases with increasing strength level. Metallic coatings, such as zinc, on low-carbon, martensitic steels can promote hydrogen stress cracking by generating hydrogen through galvanic action.

18. L.M. Dvoracek, 'Pitting Corrosion of Steel in H₂S Solutions', "Corrosion", Volume 32, No. 2, February, 1976
-

Laboratory experiments were designed to determine if steels with a black oxide surface (mill scale) pitted in the presence of chlorides. The pitting potential was found to be independent of pH between 3 and 6, where the greatest pitting was observed. However, it was concluded that pitting also could occur at a higher pH. It was determined that chlorides were necessary to cause pitting in H₂S solutions. (However, experimental times were very short and it is known that an incubation time is required to initiate pitting.)

19. Asahi Kawashima, Koji Hashimoto, and Saburo Shimodaira, 'Hydrogen Electrode Reaction and Hydrogen Embrittlement of Mild Steel in Hydrogen Sulfide Solutions', "Corrosion", Volume 32, No. 8, August, 1976
-

Effects of strain rate, applied potential, pH, temperature and hydrogen sulphide concentration on sulphide cracking of mild steel were examined at constant strain rates. It was concluded that:

- (1) The susceptibility to hydrogen embrittlement in hydrogen sulphide solutions is higher, the lower the strain rate and pH, and the higher the cathodic polarization.

(2) The change in the concentration of H₂S has little effect on the susceptibility to hydrogen embrittlement.

(3) Susceptibility is highest at 50°C.

(4) Fractographic observations showed transgranular quasi-cleavage fracture under conditions of high susceptibility to cracking, and transgranular ductile fracture under conditions of lower susceptibility to cracking. The cracks nucleate at carbides in the pearlite, at inclusions, and/or at grain boundaries.

(5) The susceptibility to cracking increases as the amount of H₂ absorbed in a steel increases.

(6) The dissolved species which promotes hydrogen embrittlement is undissociated molecular H₂S.

20. J.A. Harris and T.F. Lemke, 'Laboratory Testing of Nickel Alloys for H₂S Service', "Materials Performance", Volume 22, No.1, January, 1983

The corrosion behavior of several Ni alloys was examined in laboratory tests to evaluate materials for H₂S service. It was concluded that hydrogen charging lowered the ductility, as measured by reduction of area, in tensile tests. There was also a decrease in elongation at failure but the tensile strength was relatively unaffected. The Incolloys and Inconels showed good resistance to H₂S with the Incolloys being superior. Annealed materials in the 210 to 410 MPa region tended to be the most resistant to hydrogen embrittlement and the age hardenable, the least resistant.

21. J.A. King and P.S.C. Badelek, 'Performance of Valve Materials in Wet H₂S and CO₂ Contaminated Hydrocarbons', "Materials Performance", Volume 22, No. 1 January, 1983

This Case History describes the performance of valves and associated equipment in wet H₂S and CO₂ to NACE LF-166 prior to 1975 and to NACE-MR-01-75 since 1975. Only one body bonnet failure was reported and that involved welding. The weld configuration was poor and hardness was found to be Rc 41 in the HAZ and Rc 34 in the weld (SSCC).

Valve seats of 13 Cr with hardness often exceeding Rc 22 displayed numerous body seat cracks and, also, cracks in the shoulders of wedges.

SSCC failures of K Monel stems have been experienced with hardness above the Rc 35 max, recommended by MR-01-75.

Ball Valve Guide and Drive Pins failed due to SSCC because of high hardness (Rc 41). Case-hardened pins also failed. They were replaced with high Ni alloys to eliminate the problem. 300 series stainless steel overlaid with hardfacing material and then post weld heat treated at 900 to 950°C also have been used successfully.

Springs in valves have suffered numerous failures. A flexible epoxy coating has helped to increase life.

Bellows were changed to high Ni alloys.

Bolting was found not to conform to NACE MR-01-75.

Plating of balls in ball valves was not controlled.

This article concluded that a good Q.A. program to check manufacturers is absolutely essential. Independent inspection is incorporated in such a program.

22. Ronald N. Duncan, 'Performance of Electroless Nickel Coated Steel in Oil Field Environments', "Materials Performance", Volume 22, No.1, January, 1983

Details are given of test programs establishing the corrosion and erosion resistance of electroless nickel coating in saline/CO₂/H₂S petroleum production environments at temperatures up to 180°C.

Properly applied electroless nickel coatings can reduce or eliminate corrosion on carbon steel components in petroleum production environments. However, care must be exercised to ensure adequate thickness and proper heat treatment. In general, heat treatment of the electroless coating resulted in reduced corrosion protection due to the conversion of phosphorus to nickel phosphide. In addition, shrinkage cracks occurred allowing the corroding species to attack the metal substrate. Coatings must be tested individually for a specific environment.

23. Jan Oredsson and Sven Bernhardsson, of Sandvik AB, Sandviken, Sweden, 'Performance of High Alloy Austenitic and Duplex Stainless Steels in Sour Gas and Oil Environments' - Paper 126 presented at NACE Corrosion 1982, Houston, March 22-26, 1982

Stress Corrosion cracking tests were conducted on cold worked duplex (austenitic/ferritic) and high nickel austenitic alloys in solutions representing downhole conditions - i.e. chloride contaminated hydrocarbons containing high quantities of H₂S and CO₂. The austenitic alloy was found to resist cracking but the cold worked duplex alloy experienced cracking. The threshold stress to produce cracking in the duplex alloy decreased with increasing cold work and with decreasing pH. Increasing temperature tends to counteract the effect of the cold working.

24. William C. Mack, Gary Molitor and Jerry D. Gottschling of Babcock & Wilcox, (U.S.A.) 'H₂S Testing of Specialty Steels for Oil Country Tubular Applications' - Paper 184 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981

Low alloy steels (low Cr and Low Mo steels of the 4130, 4135 variety) and some high alloys (over 9% Cr) were tested for resistance SSCC. It was found that the low alloys showed good sulphide cracking resistance but this resistance depended

primarily on microstructure. A fully tempered martensitic structure exhibited the best resistance.

Also, it was determined that the size of the test specimen influenced the test results. High chromium alloys in the overaged condition exhibited the best SSCC resistance as heat treatment was important.

25. C.M. Hudgens, R.L. McGlasson, P. Mahdizadeh and W.M. Rosborough of Continental Oil, Research Dept., 'Hydrogen Sulfide Cracking of Carbon and Alloy Steels', "Corrosion", Volume 22, August, 1966 (Classic Paper)

An extensive examination was made of sulphide cracking of carbon steel. Parameters such as hardness, yield strength, stress and microstructure along with sulphide concentration and pH were studied. It was found that time to failure was a reliable means of testing for cracking studies. Cold working should be limited to prevent cracking, i.e. control the amount of straightening following heat treatment. Strength limits alone for alloy steels will not prevent cracking. Cracking essentially stopped when the pH reached 9.5. Martensitic structure is not necessary for a steel to be susceptible to cracking.

Primary Conclusions Were:

- (1) No material tested except K-Monel can resist SSCC at strength levels above 689.5 MPa (100,000 psi).
- (2) There is a minimum hardness below which cracking does not occur for a given stress condition. This hardness increases with decreasing H₂S concentration.
- (3) There appears to be no hardness below which failure will not occur under very severe conditions of stress, cold work, and high H₂S concentration.
- (4) The time to failure increases with decreasing hardness, decreasing stress and decreasing H₂S concentration.
- (5) At low hardnesses and/or low H₂S concentrations cracking occurs only at applied loads near or above the yield stress.
- (6) Somewhat higher usable strength levels are attained from quench and tempering than from normalizing.
- (7) At higher solution H₂S concentration (above 30-50 ppm), cracking occurred within a few days or not at all.
- (8) Test exposures approaching service life may be required to obtain truly representative data on trace H₂S studies.
- (9) The pH of the H₂S containing solutions does not exhibit a very marked effect until decidedly alkaline values are obtained.

This paper was written some time ago but its' conclusions are still largely valid. Field experience with failures at hardness levels below Rc 22, reports

of the good performance of quenched and tempered structures and accounts of the rapidity of failure, all attest to the quality of this work.

26. B.E. Wilde, C.D. Kim and E.H. Phelps, 'Some Observations on the Role of Inclusions in the Hydrogen Induced Blister Cracking of Line Pipe Steels in Sulfide Environments' - Paper 7 presented at NACE Corrosion 1980, Chicago, March 3-7, 1980
-

The investigation studies the effects of hydrogen blister cracking on steels in solutions simulating process conditions and in the BP test. It was concluded that Type II MnS inclusions were the predominant initiation sites for cracking but glassy silicates and massive columbium carbonitrides also could act as initiation sites. Hydrogen blister cracking was found to be strongly influenced by the concentration of H₂S, suggesting a threshold fugacity below which blistering will not occur. This threshold level is felt to be between 10⁴ to 10⁵ atmospheres. Propagation of hydrogen-induced blister cracking occurs by hydrogen-assisted fracture of the matrix surrounding the initiating inclusions.

Step-wise, hydrogen-induced blister crack propagation occurs by hydrogen assisted fracture between interconnecting planes.

27. T.V. Bruno and R.T. Hill, Metallurgical Consultants, 'Step-Wise Cracking of Pipeline Steels - A Review of the Work of Task Group T-1F-20' - Paper 6 presented at NACE Corrosion 1980, Chicago, March 3-7, 1980
-

A reason is given for the formation of Task Group T-1F20, i.e., to produce a standardized test to detect step-wise cracking in pipeline steels. A proposed test is included. This version is identical to the BP test except that the pH is to be recorded only. No control had been imposed at this point.

28. Gunter Herbsleb, Rolf K. Popperling and Wilhelm Schwenk, Mannesmann Research Institute, West Germany, 'Occurrence and Prevention of Hydrogen-Induced Step-Wise Cracking and Stress Corrosion Cracking of Low-Alloy Pipeline Steels' - Presented as Paper 9 NACE Corrosion 1980, Chicago, March 3-7, 1980
-

The study involves the effects of various solutions, containing H₂S at different pH levels, on steels. It was determined that cracking of higher strength, low alloy steels and lower strength steels in H₂S environments was due to Hydrogen Stress Corrosion Cracking. The maximum susceptibility to HSCC occurred at temperatures between 5 and 40°C. Degradation in low strength steels tends to be the result of HIC which occurs without the application of applied stress. One may occur without the other and resistance to one does not mean resistance to the other. HIC cracks are thought not to have any significant service restrictions unless step-wise cracking has occurred. Non-metallic inclusions are considered the prime initiation sites for blisters and their shapes are critical, i.e., long, thin ones more susceptible than round ones. In testing for HIC it is suggested that the test should be to find an acceptable level, not to find a steel that is immune.

This paper displays sound thinking and a practical approach to identifying steels for H₂S service.

29. T. Taira and Y.K. Obayashi of Nippon Kokan, 'Full Size SSC Test Result of Line Pipe Under Wet Sour Gas Environments' - Paper 183 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981
-

Sulphide Stress Corrosion Cracking tests were carried out on full size pipe samples in an attempt to simulate pipelines exposed to wet sour gas environments. The test conditions involved 80% of the Specified Minimum Yield Strength in NACE-type solutions. Both ordinary desulphurized steels and super-low sulphur, Ca - treated steels were examined. Four types of cracks - namely, straight, step-wise, sulphide stress cracks and blisters - were generated in the base metal. Initiation of HIC (straight cracks) was completed in about two weeks.

Step-wise cracks propagated continuously throughout the test but were confined within a narrow area. SSCC was found to initiate at corrosion pits and to propagate perpendicular to the hoop stress. The crack was likely to branch, then stop propagating. SSC also initiated at the centre of the blisters.

Cracks were frequently found in the ordinary desulphurized steels but seldom in the Ca-treated material.

It was determined that the NACE laboratory test, in which samples are immersed in solution, is a more severe test than conditions that simulate pipe-lines where hydrogen charging can take place from only one side. This may give a false impression that pipeline steels may fracture when, in fact, they would perform satisfactorily.

This is a good paper with both theoretical and practical considerations.

30. A.A. Omar, R.D. Kane and W.K. Boyd of Battelle Houston, 'Factors Affecting the Sulfide Stress Cracking Resistance of Steel Weldments', Paper 196 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981
-

The authors present a literature review of the effects of various parameters on the Sulphide Stress Cracking resistance of steel welds in sour environments. The higher the H₂S concentration the more likely the welds are to fail. Rc 22 is a practical limit on hardness for welds to ensure successful operation, although higher values may be used under extremely low H₂S conditions. A partial pressure of H₂S of 0.001 atm is sufficient to cause SSCC. Generally, it was found that hard spots in welds produced cracks in H₂S environments. These hard spots could be martensite or bainite. High strength welds had a greater tendency to crack.

Carbon equivalent can be used to assess structures that require post-weld heat treatment to prevent cracking. Two proposals have been made:

$$CE = C + \frac{Mn}{6} + \frac{Cr + V + Mo}{5} + \frac{Cu + Ni}{15} \text{ by the International Welding Institute}$$

or

$$CE = C + \frac{V}{10} + \frac{Mo}{15} + \frac{Mn + Cr + Cu}{20} + \frac{Si}{30} + \frac{Ni}{60} \text{ by Japanese scientists}$$

If CE is below 0.35 the cracking tendency of welds is greatly reduced.

With respect to the joint design, as the constraint increases, susceptibility to SSCC also increases.

Welding Consumables are extremely important as high Mn, S, can affect weld hardness. Ni is controlled to less than 1% although recent evidence suggests this is not necessary.

Annealing and/or controlled stress relief affect the weld performance in H₂S.

31. J. Kolts and A.I. Asphahani of Cabot Corporation, 'Effect of Temperature on the Chloride-Sulfide Stress Cracking of Stainless Tubulars' - Paper 99 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981
-

Chloride/sulphide cracking resistance of Hastelloy G (austenitic) and Ferralium 255 (Duplex structure) was examined at various temperatures and H₂S concentrations. Cracking resistance of the austenitic alloy was excellent under all conditions tested. The duplex structure was resistant to cracking at low temperatures and H₂S concentrations. Increasing of temperature in dilute solutions resulted in a decrease in corrosive attack and crack path. Cracks tended to be arrested by the ferrite. However, at 400°C, cracks tended to occur in the ferrite or along ferrite/austenite grain boundaries.

Increasing the H₂S concentration resulted in cracking (tended to be in the ferrite phase). Increasing temperature reduced the amount of cracking.

Increasing the acidity in high H₂S solutions resulted in cracks in both phases over the entire temperature range studied.

Coupling Ferralium to carbon steel resulted in improved cracking resistance of the duplex alloy.

32. Glen A. Vaughn and Hung-Erh Chaung, 'Wireline Materials for Sour Service' - Exxon Research Paper 182 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981
-

Wire line materials, generally high alloys, are employed in sour environments in gas and oil wells. It was determined that alloys had to contain a minimum of 30% nickel to operate successfully for extended periods in 93°C H₂S/Cl⁻ environments. It was concluded that failure was the result of the combination of H₂S and chlorides, producing stress corrosion cracking. Coupling of the alloys resulted in protection of the more noble material.

Transgranular cracking was the predominant failure mode.

33. W.A. Bonner of Shell Oil Company, 'You Can Stop Hydrogen Attack - Special Report on Corrosion', "Petroleum Refiner", July, 1958
-

This article outlines air injection as a means of stopping hydrogen damage in high pH, H₂S solutions containing cyanides. Causes of H₂ attack are listed:

- (a) a steel surface subject to corrosion,
- (b) a source of reactive hydrogen,

- (c) a liquid water phase,
- (d) sulphide ion or other steel surface poisoning agent to stop atomic hydrogen combining to form molecular hydrogen,
- (e) imperfections or slag inclusions in the steel, and
- (f) a promoter to maintain an active steel surface.

Conditions promoting hydrogen attack are given:

- (a) low pH,
- (b) high pH under oxygen-free conditions, or
- (c) high pH in a system which contains cyanide.

34. G.M. Pressouyre, L. Bretin and CC. Zmudzinski of Creusot-Loire Research Centre, France, 'New Steels for Use in H₂S Environments' - Paper 181 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981

Two steels for oil field equipment were tested at various strength levels and compared with comparable materials permitted in NACE MR-01-75. Essentially the two alloys, Virgo 38 (similar to 17-4PH) and 2.5 PDOV Steel (similar V modified Cr-Mo steel), showed superior resistance to SSCC. Heat treating was critical as quenched and tempered structures were required.

35. C.C. Nathan, C.L. Dulaney and M.J. Leary of Betz, 'Prevention of Hydrogen Blistering and Corrosion by Organic Inhibitors in Hydrocarbon Systems of Varying Composition', "Technical Paper 219 Hydrogen Blistering and Corrosion"

Corrosion effects of H₂S are summarized.

(1) At a pH level below 4.5, acid corrosion and hydrogen blistering occur. Both increase in severity with decreasing pH. Hydrogen penetration occurs because of poisoning of the surface by sulphide ions.

(2) In the pH range of 4.5 to 6.0, because of low concentration of both hydrogen and bisulphide ions, low rates of corrosion and hydrogen penetration occur.

(3) The least protective sulphide films are formed at pH 6.0 to 8.0. These films consist of Mackinawite (FeS, previously called Kansite). If the film is broken mechanically, corrosion may occur.

(4) At a pH level above 8.0, in the absence of cyanide ion, very low corrosion rates occur because of the protective sulphide film. In the presence of cyanide ion, hydrogen blistering and corrosion can occur. However, even at this elevated pH level, cyanide ion is very strongly absorbed on steel; the heat of absorption is approximately 20 KJcal/mole. Cyanide ion also dissolves sulphide films to give iron-cyanide complex ions.

Conclusions:

(1) There seem to be no major differences in uninhibited hydrogen sulphide corrosion either with or without oil.

(2) Oil-soluble inhibitors in acid systems generally inhibit both hydrogen penetration and corrosion.

(3) Tests at the intermediate pH level were inconclusive as the uninhibited corrosion rates were not high.

(4) At pH values above 8, in the presence of cyanide, corrosion rates can be fairly high. The difference in effectiveness between oil-soluble and water-soluble inhibitors may be a function of solubility, but is probably determined by other chemical considerations in the inhibitor molecules.

However, inhibitors that prevent overall attack may not prevent hydrogen blistering and vice versa.

This is an excellent summary paper.

36. M. Meron, W. Reginiano, B. Triguboff and M. Ungarish of Israel, 'Device for Non-destructive Measurement of Hydrogen Permeation in High Strength Steels', "Metal Progress", Volume 120, No. 2, July, 1981

The article describes a method of monitoring the amount of hydrogen diffusing through steel. Hydrogen dissolving in an electrolyte generates a current that can be measured. Intensity of the current indicates the amount of H₂.

This device or other versions of it is used successfully. The paper resembles a sales pitch.

37. W.A. Bonner, H.D. Burnham, J.J. Conradi and T. Skei of Shell Oil and Shell Development, 'Prevention of Hydrogen Attack on Steel in Refinery Equipment' Paper presented to American Petroleum Institute's Division of Refining, May 12, 1953, New York, U.S.A. (Classic Paper)

Extensive damage to steel equipment through hydrogen blistering and fissuring can be sustained when streams, which contain ammonia and hydrogen sulphide at a pH of 7 to 9, are processed. Both hydrogen penetration and corrosion can be eliminated by the addition of ammonium polysulphide or oxygen to the system. Cyanide or hydrogen cyanide catalyzes the attack of the steel and can convert the polysulphide to thiocyanate, destroying its inhibitive action.

Blisters in steel walls in vessels were typically up to 75 mm (3") in diameter and were found to contain 99% H₂.

Conditions necessary for attack are given in the abstract of Ref. 33.

Methods for Controlling Hydrogen Penetration:

- (a) alter the corroding surface - clad it, paint it, condition it,
- (b) eliminate the source of reactive H₂,
- (c) eliminate liquid-water phase,
- (d) eliminate poisoning agents - this is not practical,

- (g) use cleaner steels - but it is the distribution, not the number of inclusions, that cause the problem,
- (f) control temperature - increasing the temperature increases the rate of H₂ charging and this could cause cracking following a sudden cool-down.

This information is a bit dated but still relevant.

38. T. Skei and A. Wachter of Shell Development, W.A. Bonner and H.D. Burnham of Shell Oil, 'Hydrogen Blistering of Steel in Hydrogen Sulfide Solutions' - "Corrosion", Volume 9, No. 5, May 1953
-

Extensive damage to some refinery equipment occurred due to the transmission through steel of hydrogen developed during corrosion of the steel by hydrogen sulphide solutions. Damage in the form of hydrogen blistering, fissuring and embrittlement has been particularly severe in catalytic cracking gas plants. Laboratory studies, measuring the volume of hydrogen that passed through the steel, were conducted to determine the effect of hydrogen sulphide concentration, organic acids, ammonia and hydrogen cyanide on the process. The studies indicated that transmission of hydrogen virtually ceased in some environments, probably due to the formation of a protective sulphide layer. However, in certain alkaline solutions containing cyanide ions, a high rate of hydrogen transmission continued, probably due to the formation of a ferrocyanide complex that prevented formation of a protective scale.

Low pH resulted in coating removal and higher transmission rates.

Both temperature and pressure seemed to be negligible in the transmission rates as was the steel thickness.

Oxygen was found to act as both a promoter and an inhibitor of hydrogen transmission. It was a promoter in low pH solutions and an inhibitor in high pH.

Hydrogen blistering might be prevented by use of ultra clean steels but this was felt to be impractical. High alloy steels could be used.

Again, some of the information is dated.

39. Ernest F. Ehmke of Tosco Corp. California, 'Use Ammonium Polysulfide to Stop Corrosion and Hydrogen Blistering' - Paper 59 Presented at NACE Corrosion 1981, Toronto, April 6-10, 1981
-

A summary was made of where and how blistering occurs in Fluid Catalytic Cracking Plants with some inspection recommendations included. The author claims that there have been no failures from blistering but this is incorrect. This paper restates work done by Shell personnel many years previously.

40. W.A. Bonner and H.D. Burnham of Shell, 'Air Injection for Prevention of Hydrogen Penetration of Steel' - Paper presented to the Eleventh Annual Conference NACE, Chicago, March 7-11, 1955
-

This paper describes experiments conducted with varying amounts of oxygen addition to control hydrogen penetration and subsequent blistering of steels in

alkaline solutions containing cyanides at pH over 7. Sulphide coatings on the steel were unable to prevent attack. Hydrogen probes were found to be the most successful method of detecting attack. Protection of the steel is due to the formation of a hydrogen sulphide/polysulphide film.

41. A. Ikeda, T. Kaneko and F. Terasaki of Sumitomo, 'Influence of Environmental Conditions and Metallurgical Factors on Hydrogen Induced Cracking of Line Pipe Steel' - Paper Number 8 presented at NACE Corrosion 1980, Chicago, March 3-7, 1980
-

To protect material from HIC in wet H₂S environments it was suggested that one consider C_o, the hydrogen absorbed from the atmosphere, and C_{th}, the threshold hydrogen content to cause cracking. If C_o is greater than C_{th}, cracking occurs. Factors that influence C_o are the presence of water vapour, chemical inhibitors and alloying elements. Factors that influence C_{th} are metallurgical: segregation, shape control, and microstructures.

Influence on C_o:

- (1) Cu over 0.2 wt % helps prevent H₂ absorption at pH over 4.0 due to film formation.
- (2) Cobalt over 1% or Co + Cu reduces hydrogen absorption in low pH solutions due to film formation.
- (3) The amount of absorbed H₂ correlates with the corrosion rate. However, poison elements such as Se and Te result in higher absorption rates for the same amount of corrosion.
- (4) The lower the pH value the more H₂ is generated and absorbed.
- (5) The higher the partial pressure of H₂S and CO₂, the more severe is the environment.

This article strongly recommends Cu and Co additions to steel to prevent HIC. Other studies suggest Cu and Co are effective in certain mild environments.

42. T. Taira, Y. Kobayashi, H. Inaguki, and T. Watanabe of Fukuyama Research Laboratory, 'Sulfide Corrosion Cracking of Linepipe for Sour Gas Service' - Paper 171 presented at NACE Corrosion 1979, Atlanta, Georgia, March 12-16, 1979
-

Laboratory tests conducted with a number of variables revealed the following:

- (1) HIC initiates at elongated MnS inclusions and tends to propagate along pearlite bands or the low temperature transformation microstructure associated with segregation. Desulphuring, inclusion shape control, reduction of Mn and quench-and-temper heat treatment should reduce susceptibility to HIC.
- (2) HIC tests in NACE solution (pH 3.5 - 3.8) show higher susceptibility than in BP solution (pH 5.1 - 5.3). Cu effectiveness is restricted to pH 5 or greater. Tests should be conducted at anticipated pH ranges.

(3) HIC does not develop in weld metal.

(4) NACE tensile test shows more reliable results than the Shell test due to specimen thickness differences. There is some correlation between the ratio of threshold stress to yield stress (σ_{th}/σ_y) in the NACE tensile test and average crack length (a) in the HIC test.

(5) Quench-and-tempered steel has the best resistance to SCC in both the Shell Test and the NACE Tensile Test. There is some difference in σ_{th}/σ_y between the longitudinal and transverse direction caused by elongated inclusions in the rolling direction.

(6) Hardness regions in HAZ comprise two zones - one that is tempered by the following welding pass and one that is not close to the last bead.

(7) The hardness of the HAZ depends upon the carbon equivalent and the welding parameters. Quench-and-tempered material reduces the carbon equivalent. This statement was likely translated incorrectly.

(8) The most hardened position in the HAZ is the most susceptible to SSCC. If stress-relief cannot be performed, then welding, from the outside only, should be performed.

(9) Critical hardness under stress was found to be Rc 22 for 1 atm partial pressure of H₂S. This hardness could be increased marginally for lower pressure of H₂S so Rc 22 is a safe limit.

(10) Blister growth continues for two weeks and crack propagation for four weeks in full size tests.

(11) The acceleration of HIC depends on the ratio of specific volume of solution to surface areas of the specimen. The amount of HIC in the standard HIC specimen after 4 days roughly corresponds to that in a full size pipe after 4 weeks.

(12) Susceptibility of materials to HIC in full size tests is the same as in laboratory size samples.

(13) High tensile residual stresses in longitudinal and transverse directions in girth welds did not introduce cracking perpendicular to the thickness direction.

This paper is considered one of the best produced by this group of prolific authors.

43. T. Taira, K.T. Sukada, Y. Kobayashi, H. Inagakii, and T. Watanabe of Nippon Kokan, 'Sulfide Corrosion Cracking of Linepipe for Sour Gas Service', "Corrosion", Volume 37, No. 1, January, 1981

This article is very similar to Reference 42 above.

Laboratory tests lead to much the same conclusions as in the above paper. However, it was determined that SSC was related to HIC as the main crack usually connected pre-existing planar-oriented cracks and a subsidiary crack. This subsidiary crack often initiated at a second phase particle such as pearlite.

SSC and HIC are related in the NACE Tensile Test.

HIC is presumed to occur when hydrogen atoms, generated at the steel surface by corrosion, penetrate the steel and are trapped at the interface between the steel matrix and non-metallic inclusion. When the internal pressure of molecular hydrogen at the interface exceeds a critical value, HIC initiates. MnS, alumina and niobium carbonitrides are possible initiation sites. HIC tends to propagate along segregation bands such as bainite or island martensite.

Cu additions can reduce HIC due to the formation of FeS or mackinawite on the steel surface, thereby reducing corrosion. This is only effective at pH above 4.8.

Sulphur cannot be completely eliminated so some HIC will occur. Sulphide shape control through Ca treatment is effective in preventing HIC.

Quench-and-tempered structures are best for preventing HIC.

HIC does not occur in weld metal.

In SSC the σ_{th} in the NACE test shows a relationship to the average crack length in the HIC. This is contrary to the findings of other authors.

Girth welded joints are the most susceptible to HIC because of hard spots in the HAZ. Perhaps the authors meant SSC.

44. J.C. Turn Jr., B.E. Wilde and C.A. Troianos, 'On the Sulfide Stress Cracking of Line Pipe Steels', "Corrosion", Volume 39, No. 9, September, 1983

Constant load tests in hydrogen sulphide saturated, 5% sodium chloride/0.5% acetic acid solution (NACE Tensile Test) were conducted on several line pipe steels to show that such steels can and do fail by sulphide stress cracking. Steels showing excellent resistance to HIBS in the BP test, were also found to fail rapidly in the NACE test, suggesting that resistance to HIBS does not necessarily mean SSC resistance. The mechanism of SSC in low strength steels was shown to be hydrogen embrittlement. The susceptibility to hydrogen embrittlement was found to be inversely proportional to the hydrogen input fugacity.

The authors suggest caution in the use of Rc 22 as a controlling factor as it appears that failure is a matter of environment severity and applied stress, not of the tensile properties (or hardness) of line pipe steels. This is apparent in Case Histories, Reference 164.

45. A. Ikeda, T. Kaneko and F. Terasaki, 'On the Mechanism of Hydrogen Induced Cracking of Line Pipe Steel in Wet Hydrogen Sulfide Environment', "Environmental Degradation of Engineering Materials", Blacksburg, Virginia, 1981
-

It is proposed that HIC of pipeline steel is related to the hydrogen concentration for HIC (Cth) and to the absorbed hydrogen concentration (Co). These are related to the lattice-dissolved, hydrogen concentration and correspond to the equilibrium pressure induced at the cracking site. If Co is less than Cth cracking does not occur. If Co is greater than Cth then HIC occurs through hydrogen embrittlement. To protect pipeline steels Co must be lowered and Cth elevated.

46. R.S. Treseder, 'Guarding Against Hydrogen Embrittlement', "Chemical Engineering" June 29, 1981
-

This article discusses sulphide stress cracking and hydrogen blistering. It points out that free-machining steels are more susceptible to SSC than other steels of the same strength level. Materials selection is the major method of controlling SSC. In-plant monitoring involves H2 patch probes. Somewhat dated for 1981, this article was more applicable about 1971.

47. R.L. Piehl of Standard Oil of California, 'Corrosion By Sulfide-Containing Condensate in Hydrocracker Effluent Coolers' - Paper presented to American Petroleum Institute's Division of Refining, Philadelphia, May 15, 1968
-

Erosion/corrosion was recorded due to excessive velocities of alkaline solutions and to the conversion of sulphide and ammonia to various compounds including H2S. Velocities should have been limited to less than 9 m/sec (30 ft/sec).

48. G.J. Biefer, 'Sulfide Stress Cracking Behaviour of Some "Big-Inch" Line-Pipe Steels', "Corrosion", Volume 32, No. 9, September, 1976
-

As part of an investigation of 762-1218 mm (30-48") diameter line-pipe of 462-579 MPa (67-84 Ksi) pipe for a proposed arctic pipeline, SSC tests were performed using U-bend samples. Cracks were found to initiate in the "most susceptible" microstructure for each steel, generally in the HAZ where quenching produced hard spots. Failures were encountered in areas with hardness less than Rc 22 but a detailed analysis was not made to determine the effects of strain and detailed microstructure.

49. R.D. Kane, M. Watkins, D.F. Jacobs, and G.L. Hancock of Exxon Research, 'Factors Influencing the Embrittlement of Cold Worked High Alloy Materials in H2S Environments', "Corrosion", Volume 33, No. 9, September, 1977
-

High nickel alloys, notably Hastelloy C-276, Inconel 625, and MP35N, have all shown exceptional resistance to weight loss corrosion in H2S containing solutions. These alloys, and Hastelloy C4 were all tested as tubing in H2S environments. The tube samples, received in the cold reduced condition, were subjected to various heat treatments from 148 to 593°C (300 to 1100°F) for times ranging from 10 minutes to 500 hours. The effect on cracking susceptibility of the following were studied:

- (a) cold working,
- (b) aging time and temperature,
- (c) sample orientation
- (d) galvanic coupling with steel, and
- (e) environmental temperature and composition.

It was found that aging for very short periods at high temperatures or for longer times at lower temperatures reduced the resistance of the alloys to hydrogen embrittlement. Failures were limited to samples that were coupled to steel and stressed in the transverse direction. No failures were found in longitudinally stressed samples nor in transversely loaded specimens without steel couples. Elevated temperature reduced susceptibility to cracking.

50. A. Joshi of Physical Electronics Industries Inc., Minnesota, 'Influence of Density and Distribution of Intergranular Sulfides on the Sulfide Stress Cracking Properties of High strength Steels', "Corrosion", Volume 34, No. 2 February, 1978
-

Scanning Auger microprobe analysis was used to determine grain boundary precipitates and second phases on fresh fracture surfaces of sulphide cracking failures. It was determined that a thin film of (Fe, Mn)S or P present at grain boundaries increases the SSC susceptibility of the material.

51. Bruce D. Craig of Marathon Oil Company Research Centre, 'A Contribution to the Mechanism of Hydrogen Entry into Steels in Acid Environments', "Corrosion", Volume 34, No. 8, August, 1978
-

The dissolution of sulphide inclusions in steels, when exposed to acid media, creates an environment similar to those containing H₂S, and, as a result, increased charging of hydrogen occurs. Spherical inclusions should reduce the available absorption sites. Mn-rich inclusions may enhance hydrogen entry while Ti and Cu additions should inhibit hydrogen penetration.

52. B. Stellway and H. Kaesche of Federal Republic of Germany, 'Rate Controlling Steps of SSC of High Strength Steels', "Corrosion", Volume 35, No. 9, September, 1979
-

SSC tests of high strength steel have confirmed that absorbed hydrogen is the damaging species. This assumes that lattice decohesion of the metallic bonds by absorbed hydrogen is a fundamental feature of the cracking process.

The study revealed that SSC cracks propagate discontinuously along the former austenite grain boundaries.

Two theories for Hydrogen Embrittlement are considered:

- (a) precipitation of molecular hydrogen in microvoids (by Zapffe and Sims), and
- (b) reduction of cohesive force of the metallic bonds caused by absorbed H₂ (by Troiano).

Probably, a combination of the two is responsible for hydrogen embrittlement.

53. B.J. Berkowitz and R.D. Kane of Battelle, Houston and Exxon Research, 'The Effect of Impurity Segregation on the Hydrogen Embrittlement of a High Strength Nickel Base Alloy in H₂S Environments', "Corrosion", Volume 36, No. 1, January, 1980
-

Hastelloy C-276 tubulars coupled to steel were stressed (C-rings) in an aqueous NACE solution (5% NaCl, 0.5% acetic acid, saturated with H₂S). They exhibited adequate embrittlement resistance. However, moderate aging treatments in the range of 200-500°C resulted in increased susceptibility to HIC. Grain boundary compositions were studied, using Scanning Auger Spectroscopy and it was found that considerable phosphorus segregation to the boundaries had occurred. Experimental low phosphorus heats showed improved resistance to hydrogen induced cracking and embrittlement. It was observed that both grain boundary phosphorus concentration and hydrogen embrittlement susceptibility increased with aging severity. Also, resistance to hydrogen embrittlement increased as bulk phosphorus concentration decreased.

54. R.D. Kane and B.J. Berkowitz of Battelle, Houston and Exxon Research, 'Effect of Heat Treatment and Impurities on the Hydrogen Embrittlement of a Nickel Cobalt Base Alloy', "Corrosion", Volume 36, No. 1, January, 1980
-

A high strength nickel-cobalt base alloy (MP35N) was examined in an aqueous NACE solution to determine the effects of impurities (resulting from heat treatment) on the hydrogen embrittlement behaviour. The alloy initially was in the cold worked condition. The studies revealed that aging in the temperature range of 204 to 593°C decreased resistance to hydrogen embrittlement while higher temperature ranges, 697 to 816°C, improved resistance while maintaining the high strength. Scanning Auger analysis of hydrogen embrittled fracture surfaces indicated that concentration of P and S impurities on the major crystallographic boundaries contributed to the effect.

Fracture was predominantly intercrystalline along major crystallographic interfaces (twin boundaries and grain boundaries). It was not determined whether both P and S are damaging or just one of them. Severe cold working probably contributed to the segregation as one would normally not expect much segregation at the low temperatures.

55. G.J. Bieffer, 'The Stepwise Cracking of Line - Pipe Steels in Sour Environments', "Materials Performance", Volume 21, No. 6, June, 1982
-

Results of a literature survey on step-wise cracking are presented. This is a good document for references.

56. A.J.R. Rees, 'Problems with Pressure Vessels in Sour Gas Service (Case Histories)', "Materials Performance", Volume 16, No. 7, July, 1977
-

This is an excellent article relating case histories of failures in pressure vessels due to H₂ blistering. The case histories are listed here.

Amine Contactor (A Type Scrubber) - A vessel constructed of ASME A-212 FBO of varying thickness, was designed to scrub H₂S from natural gas using mono-ethanolamine (MEA), changed in 1965 to diethanolamine (DEA). Hydrogen blistering was found in 1971 in 100 mm (4") thick shell below the bottom tray, above the liquid level. Blisters were fairly large with one being about 160 cm². The inside surface, bulged about 6 mm, contained a circumferential crack, 100 mm long. U.T. inspection revealed areas of segregation.

During preheating to repair vessel, 50 new blisters appeared. The vessel was repaired by venting blisters, welding plate on outside (vent holes provided), gouging out blisters and filling with weld metal. A 316 SS liner was applied on the inside. The system was stress relieved.

2nd Amine Contactor of A516 Grade 70 built in 1972 - Blisters were discovered after 2 years and a 1.85 m section was replaced.

Primary Sulfinol Contactor - Hydrogen Laminations were found in a sulfinol primary contactor built in 1966 after 8 years' service. Two areas, 36 x 91 cm and 25 x 100 cm, were found. Holes were drilled into the areas from the outside and fitted with gauges to monitor H₂ activity. Ultrasonic examination was carried out on shell at 6 month intervals.

Hydrogen Blistering in the Sulfinol Flash Tanks - Erosion of the iron sulphide layers lead to hydrogen blistering and replacement of sections.

Hydrogen Blistering in Inlet Chiller Separator Vessel - The vessel was built of ASME SA 516 Grade 70 in 1970. In 1974 H₂ blisters were discovered along the top centre of the horizontal vessel. The blisters were up to 150 mm in diameter. Laminations were extensive as shown by U.T. examination. Ruptured vessels were repaired by welding. Vent holes were drilled from the outside to segregation areas. The holes were fitted with pressure gauges. The interior of the vessel was coated with epoxy as a temporary measure.

Hydrogen Blistering in Amine Regenerator Tower - Hydrogen blistering was encountered in the 12.5 mm (1/2") wall of a regenerator tower after about 8 years' service. The blisters were about 150 mm in diameter. The affected section was replaced and the inside lined with gunite.

The author concludes that many of the problems encountered with the pressure vessel, occurred during shutdown or start-up conditions.

57. G.C. Schmid of Armco Inc. Research, 'The Resistance of Nickel Containing Steels and Weld Metals to Sulfide Stress Corrosion Cracking', "Materials Protection", Volume 19, No. 4, April, 1980

NACE MR-01-75 limits the amount of nickel in welds and alloys for H₂S service to less than 1% to prevent SSC. The author tested steels and welds containing 0,

1 3/4% Ni, 2% Ni and 3 1/2% Ni and found no evidence to suggest that Ni had any effect upon the SSC resistance of the alloys. (However, laboratory-produced welds might well show no effects. In addition, the environment may play a key role and this has been overlooked.)

58. A.K. Dunlop of Shell Development Co., 'Discussion on The Resistance of Nickel Containing Steels and Weld Metals to Sulfide Stress Corrosion Cracking', "Materials Performance", Volume 19, No. 8, August, 1980
-

The author states it would be premature to drop the 1% Ni requirement for H₂S service based on the evidence of the above paper. Too many other authors have found opposite results. It is suggested that two mechanisms are at work, depending primarily on the environment. These two mechanisms may be interactive. Further studies are needed.

59. Herbert H. Uhlig of Woods Hole Oceanographic Institution, 'Effect of Aqueous Sulfides and Their Oxidation Products on Hydrogen Cracking of Steel', "Materials Performance", Volume 16, No.1, January, 1977
-

Data presented on the cracking of steel in sea water indicates that as little as 2 ppm of S in solution causes rapid cracking, suggesting a hydrogen cracking test may be useful. H₂S appears to be the responsible poison that drives hydrogen into the steel.

60. F. Borik, O.R. Anselme, B. de Sivry, P. Bouseel and C. Bonnet of Climax Molybdenum and Compagnie Francaise des Petroles, France, 'Sulfide Stress Cracking Resistance of Electron Beam Welded, High Strength Ni-Cr-Mo Line Pipe Steels', "Materials Performance", Volume 22, No. 2, February, 1983
-

Compagnie Francaise des Petroles has developed a technique for laying large diameter gas piping at the bottom of the sea. This technique involves fabrication using an electron-beam welding technique. Consequently, tests were to determine whether or not the susceptibility to SSC determined for other types of welds was applicable in this case.

Three strength levels were tested, X60, X80 and X100, after tempering at 600°C. It was found that quench-and-tempered steel structures gave the best SSC resistance and that EB welding did not affect the resistance of material to the environments. The X100 material proved to be unsatisfactory for H₂S service.

61. L.M. Dvoracek of Union Oil, 'High Strength Steels for H₂S Service', "Materials Performance", Volume 15, No. 5, May, 1976
-

It was determined that steels of the AISI 4340 variety could be made resistant to SSC by controlling the Ni, Mn and S contents. However, there were discrepancies between tables and tests in the paper. Modification of the alloy with Mo and Cb produced good resistance to SSC.

62. Wu-Yang Chu, Shi-Qun Li, Chi-Mei Haiiao and Juhug-Zuor Tien of Peking, China, 'Mechanism of Stress Corrosion Cracking of Steels in H₂S', "Corrosion", Volume 36, No. 9, September, 1980
-

A very theoretical study of the aspects of hydrogen embrittlement, this paper proposes a new mechanism for hydrogen induced SCC as follows: atomic hydrogen concentrating in front of the crack tip by stress-induced diffusion can cause delayed plastic deformation and can result in the nucleation and propagation of SCC. For low strength steels, the initial crack propagates continuously along the path near the border of the delayed, enlarged plastic zone.

For ultra-high strength steels, following closure of delayed plastic zones, stress corrosion cracks are nucleated at zone tips. These discontinuous cracks can grow to join one another.

Stress corrosion fracture caused by hydrogen-induced, delayed plasticity may be intergranular or quasi-cleavage. As strength is decreased, the mode of fracture changes from intergranular to quasi-cleavage.

The theory is very similar to Beachum's proposal made eight years earlier.

63. P.H. Pumphrey of Central Electric Generating Board, Surrey, England, 'The Role of Sulfide Inclusions in Hydrogen Entry During the Exposure of Steels to Acids', "Corrosion", Volume 36, No. 10, October, 1980
-

Studies revealed that H₂S, produced by the dissolution of (FeMn)S inclusions in various carbon steels in cathodically charged environments, increased the H₂ permeation rates into the steel. Elongated inclusions resulted in higher permeation rates than rounded ones.

64. Guenter Herbsleb and Rolk K. Poepperling of Mannesmann Research Institute, West Germany, 'Corrosion Properties of Austenitic-Ferritic Duplex Steel AF22 in Chloride and Sulfide Containing Environments', "Corrosion", Volume 36, No. 11, November, 1980
-

Although tests were carried out in sulphuric acid with various additions, the results involving H₂S are valid for the present study. Generally it was determined that chloride must be present in combination with H₂S to cause SSC. Failure is by transgranular cracking with the cracks initiating at corrosion pits. SSC can be alleviated by lowering the stress level below 60% of yield.

65. D.V. Sdyanarayane Gupta of Gulf South Research Institute, 'Corrosion Behaviour of 1040 Carbon Steel - Effect of pH and Sulfide ion Concentrations in Aqueous Neutral and Alkaline Solutions at Room Temperature', "Corrosion", Volume 37, No. 11, November, 1981
-

Tests conducted at pH levels of 6 to 14 indicated that corrosion rates due to sulphides were higher at lower pH levels. In addition, the metal undergoes pitting as well as general corrosion. This pitting can affect the structural ability of the metal even under low general corrosion rates.

66. R.J. Twigg, 'Material Failure - Fact or Fiction?', "Canadian Chemical Processing", Volume 64, No. 1, February 6, 1980
-

This case history describes a failure of a flare header due to sulphide pitting.

67. Juri Kolts, James B.C. Wu and Aziz I. Asphahani, 'Highly Alloyed Austenitic Materials for Corrosion Service', "Metal Progress", Volume 124, No. 4, September, 1983
-

High nickel alloys such as Incoloy 825, Hastelloys G-3 and C-276 are highly resistant to SSC in sour environments in the absence of oxygen. They become susceptible to cracking in deaerated solutions only after the addition of mineral acids or acid salts. Similarly, the presence of elemental sulphur increases the tendency to SSC in sour environments.

68. V.N. Kudryavtsev of Academy of Sciences, Moscow, Kh.G. Schmitt - Thomas, W. Stengel and R. Waterschek of Technische Universitat, Munchen, Germany, 'Detection of Hydrogen Embrittlement of a Carbon Steel by Acoustic Emission' submitted for publication, 1980
-

Both hydrogen charged and uncharged steels were loaded in tension and were monitored with acoustic emission monitoring. Differences in material response were detected and it was postulated that acoustic emission could be used to detect hydrogen embrittlement. See Reference 179 for a more detailed discussion of a similar paper.

69. O. Vosikovsky and A. Rivard of Canmet, 'The Effect of Hydrogen Sulfide in Crude Oil on Fatigue Crack Growth in a Pipe Line Steel', "Corrosion", Volume 38, No. 1, January, 1982
-

Experiments revealed that high levels of H₂S in crude oil resulted in substantial increases in fatigue crack growth rates at lower H₂S levels. See Reference 188 for a more detailed discussion of a similar paper.

70. Yuichi Yoshino of The Japan Steel Works, Hokkaido, Japan, 'Low Alloy Steels in Hydrogen Sulfide Environment', "Corrosion", Volume 38, No. 3, March, 1982
-

Extensive testing in NACE solution of a variety of low alloy steels studied corrosion, hydrogen absorption and sulphide stress cracking. It was found that nickel dramatically decreased the threshold stress but it also raised the yield strength. Molybdenum had a pronounced beneficial effect on SSC resistance, particularly in the absence of Cr. Mo improved the Charpy impact toughness but V impaired it. Cr increased the susceptibility to SSC. Carbon content was found to reduce the SSC resistance only slightly. Manganese was found to reduce the SSC resistance slightly.

All elements except copper were found to increase the corrosion rate. Copper formed a film less prone to cracking. Chromium was found to increase the amount of diffusible hydrogen about 3 times over a 0-2% chromium range.

Additions of Ti significantly raised the threshold stress whereas Nb or Nb plus Ti did not. It is proposed that SSC resistance is affected strongly by the nature of the carbide/matrix interfaces rather than by the crystalline structure of the matrix.

It is suggested that the AECB should have this paper as it is a clear discussion on the effects of alloying elements without the prejudices noted in some other papers.

71. Bruce D. Craig of Marathon Oil, 'The Effect of Nickel on Hydrogen Cracking Resistance in Low Alloy Steels - A review', "Corrosion", Volume 38, No. 9, September, 1982
-

A review of available literature has lead the author to conclude that there is no conclusive, scientific proof of the effects of Ni on the hydrogen cracking resistance. More work is needed.

72. R. Garber of Climax Molybdenum, 'Higher Hardenability Low Alloy Steels for H2S Resistant Oil Country Tubulars', "Corrosion", Volume 39, No. 3, March '83
-

Nine steels with high hardenability were evaluated for potential application as hydrogen sulphide-resistant, oil country tubulars. It was found that increasing the Mn content from 0.5% to 1.0% increased the SSCC resistance. Increasing the Cr content from 1.0 to 1.5% increased Klssc at lower strength levels (contrary to other studies). Addition of Nb had a small beneficial effect. Increase of Ni up to 1% did not lower the SSC resistance.

73. W.R. Schmeal, A.J. MacNab and P.R. Rhodes of Shell Development, 'Corrosion in Amine/Sour Gas Treating Contactors', "Chemical Engineering Processing", March, 1978
-

Three Amine/Sour Gas Treating Contactors suffered blistering and step-wise cracking in periods ranging from 10 months to 3 years. The blisters were found in areas where high corrosion had occurred. Other areas of the vessels were protected by heavy scales. Erosion had removed the scales in the attack-prone areas. Boiling which had occurred in the areas of high attack, resulted in the removal of scale.

74. Felipe Paredes and W.W. Mize, 'Hydrogen Blisters in Gas Transmission Lines and Preventative Methods', Reprinted from January, 1955 issue of "Pipe Line News" (Classic Paper)
-

In 1950, El Paso Natural Gas Company installed a 600 mm (24") trunk line with 400 mm (16") and 200 mm (8") laterals from a gas field to a treatment plant. The gas contained 15 mole % CO₂ and 1 mole % H₂S. From October 27, 1951 to January, 1952 four breaks occurred in the 600 mm (24") line and 6 breaks occurred on the 400 mm (16") lateral. Blisters associated with the breaks were noted. An analysis of the gas in the blisters indicated 94% H₂, 2% methane, with traces of CO₂ and CO. It was concluded that hydrogen blistering caused the failures so an organic inhibitor was injected into the line. Hydrogen probes

used to monitor attack on the line ceased to record H₂ as the inhibitor moved down the line indicating cessation of the corrosion that was producing the hydrogen.

The breaks generally originated in the failure of a blister and most of the blisters broke toward the inside of the pipe, against the gas pressure. In all breaks the pipe ripped in two places, 180° apart, usually at the 3 o'clock and 9 o'clock positions. The breaks followed a sinusoidal curve and passed through welds. The symmetry of the breaks was broken only when the rip went through other blisters. A herringbone pattern was evident on the fracture surface pointing back to the point of origin. All these manifestations attest to a sudden release of energy as would be expected with brittle fracture.

The authors suggest polysulphide injection might prevent failure but polysulphide is effective in very different process environments than one encounters in the pipeline and would not be effective in this case. This classic paper is extremely detailed in its treatment of the subject and is often used as a reference in subsequent work.

75. T. Taira and Y. Kobayashi of Nippon Kokan, 'Resistance of Pipeline Steels to Wet Sour Gas', - Paper presented to The First International Conference on Current Solutions to Hydrogen Problems in Steel, Washington, D.C., November, 1982
-

The effects of metallurgical factors to improve the resistance of pipeline steels to HIC and SSCC are examined. It was determined that Cu additions result in a passive film retarding corrosion with a pH of 5 or higher. This effect disappeared in lower pH solutions. Elongated MnS and clusters of Al₂O₃ were often observed on a surface fractured by HIC. Shape control by Ca treatment or rare earth metal additions are required to increase resistance to HIC.

HIC was found to propagate most easily along a low temperature transformation structure such as bainite or martensite. Mn, P, Mo and C all tended to segregate to such a microstructure, causing problems. Nb, V and Ti, all effective in increasing toughness, did not affect the microstructure in the segregation zone.

If Mn can be limited to less than 1% and C to less than 0.02%, the resultant microstructures become insensitive to hydrogen embrittlement in the segregation zone.

Full size line pipe tests were done and revealed that resistance to HIC is essential to prevent pipe damage under sour environments. Single sided charging must be used to simulate field conditions.

PRESENTATION TO CSA SOUR GAS LINEPIPE TASK FORCE by Nippon Kokan of Japan - Calgary Alberta, October 1981 - several papers and documents as follows:

76. 'Sulfide Corrosion Cracking of Welded Line Pipe in Sour Gas Service', Nippon Kokan - Technical Bulletin No. 243-074 printed in November, 1980
-

A description is given of conditions and metallurgical structures leading to hydrogen induced cracking in both the BP Test and NACE solutions. The paper summarizes most of the papers presented by Nippon Kokan to date.

77. N. Siki, T. Kotera, T. Nakasawa, Y. Kobayashi, T. Taira of Nippon Kokan, 'The Evaluation of Environmental Conditions and the Performance of Linepipe Steels Under Wet Sour Gas Conditions', submitted to NACE 1982 Conference
-

Severity of HIC of line pipe steels was evaluated using hydrogen permeation and pH variation in synthetic sea water. It was determined that the hydrogen permeation rate increases with an increase in the partial pressure of H₂S gas and CO₂ gas. The pH decreases with increases in partial pressure of both H₂S and CO₂. The effect of CO₂ on the permeation rate is smaller than that of H₂S.

78. 'Development of Line Pipes for Sour Gas Service - Part I (HIC and SSC Resistance of Line Pipes for Sour Gas Service)' - Paper presented to Task Force September, 1980
-

The NACE test was used to evaluate various conditions conducive to making line pipe resistant to HIC and SSC. It was concluded that shape control and a reduction in inclusions were necessary. Low sulphur and Ca treatment could produce material with an excellent HIC resistance. In order to suppress segregation leading to cracking, Mn should be controlled to less than 1%. If Mn exceeds 1% a quenching and tempering treatment would produce optimum resistance.

-
79. A. Ikeda, T. Kaneko, T. Hashimoto, M. Takeyama, Y. Sumitomo and T. Yamura of Sumitomo Metal Industries, 'Development of Hydrogen Induced Cracking (HIC) Resistant Steels and HIC Test Methods for Hydrogen Sulfide Service', - Paper Session 11 H₂S Symposium at the 1983 CIM Conference, Edmonton, August 22-23, 1983
-

This paper is extremely difficult to understand due to language and spelling errors. Essentially, it is a literature review of all work done in the past 10 years but errors are made in some reporting of other studies. It is concluded that hydrogen blistering is a manifestation of hydrogen-induced cracking (step-wise cracking also) and occurs in low strength steels. Sulphide stress cracking is a hydrogen embrittlement phenomenon and occurs in high strength steels. The two can work simultaneously in intermediate strength steels. HIC will not occur if the amount of hydrogen in the steel is less than that required to initiate cracking.

Single side testing of steels should be done to simulate field conditions.

Hydrogen permeation measurement in the field and in the laboratory are necessary to assess the severity of the environment as refinery corrosion appears to occur at pH 4.5-4.8 (generally considered by North American and European authors to be higher pH catalyzed by cyanides).

Steel for line pipe service at a lower pH can be produced by eliminating inclusions, producing a homogenous microstructure, and eliminating segregation.

Cu bearing steel resists HIC above 4.8 pH and Co additions help to reduce HIC at lower pH.

80. A. Ikeda, M. Nakanishi, T. Kaneko, Y. Sumitomo and M. Takeyama of Sumitomo Metal Industries, 'Improvement of Hydrogen Sulfide Cracking Susceptibility in Line Pipes for Sour Gas Services' - Reprinted from "The Sumitomo Search" No. 26, November, 1981
-

This paper outlines the results of tests to develop steels that are resistant to both HIC and SSC under varying conditions. Both parent material and welds were examined.

It was concluded that both HIC and SSCC were serious problems in line pipe service. HIC was mainly affected by inclusions and segregation. Two types of SSCC were observed. Type I occurs in the parent material or HAZ in relatively low hardness material in a ferritic structure. Small cracks parallel to the plate surface occur and propagate perpendicular to the axis of applied stress (HIC). Type II SSCC initiates and propagates directly from the stress concentration points and is associated with high hardness structures such as bainite or martensite. Small amounts of Cu addition are beneficial in preventing HIC in mild environments. Shape control of inclusions by Ca treatment is probably the most effective means of preventing HIC.

81. M.G. Hay, 'Corrosion Problems Associated with Welds at Bruce Heavy Water Plant' - CIM Conference, Session 19, Halifax, August, 1980
-

Test coupons exposed for two years in the BHWP were used to examine the effects of welding methods and consumables on corrosion. Welds in the plant piping had suffered preferential attack in both the hot and cold environments. It was determined that GTAW welds were more prone to attack than SMAW welds. The GTAW welds with E70S-2 had a less noble potential than the pipes and flanges. Additional laboratory tests revealed GTA welds generally performed more poorly than SMA welds although E70S-3 consumable was better than E70S-2. SMA welds tended to suffer micropitting. Attack was concentrated in the filler pass.

In dissimilar metal welds, cracking had been observed in the area of the fusion boundary between the carbon steel and the weld metal. No heat treating was performed as the heat from the second pass tempered the carbon steel HAZ. Cracking proceeded along the fusion boundary at the root pass of the weld but propagated into the carbon steel heat affected zone at the second pass.

With nickel base overlay, the crack propagated entirely along the fusion boundary.

Dissimilar metal welds suffered SSCC in the area of the fusion boundary between the alloy metal and the carbon steel. Cracking occurred through a hard, non-

tempering, elongated phase which formed in the austenitic weld metal, at, or close to, the fusion boundary with the ferritic material. It was unaffected by heat treatment.

This paper and the test results were used extensively in the heavy water industry as they corresponded with findings in the field.

82. M.G. Hay and D.P. Dautovich of Ontario Hydro Research, 'Corrosion of Carbon Steel at Bruce Heavy Water Plant' - NACE Eastern Regional Conference, Montreal, September 27-29, 1977
-

Excessive corrosion was found in the third stage feed and dehumidifier loops in the BHWP. Corrosion occurred in process areas where cooling from 120°C to 30°C was experienced. Maximum line thinning usually occurred immediately after a specification change from stainless steel to carbon steel with corrosion rates averaging 4.1 mm/y (160 mpy). Corrosion proceeded by means of a pitting mechanism with the pits eventually growing into one another. Studies revealed that the mackinawite form of iron sulphide which was found on the steel was easily soluble and non protective. The ferrous ion solubility was found to be temperature sensitive, increasing with a decrease in temperature. Corrosion occurred under specific conditions of low fluid velocity.

Increasing the solution pH resulted in a decrease in corrosion. Later studies identify the problem as iron transport.

83. R.J. Twigg, and H.T. DeBeer of Atomic Energy of Canada Limited, 'Corrosion of Steels in an H₂S Environment' - NACE Eastern Regional Conference, Montreal, September 27-29, 1977
-

Problems associated with various materials at the GBHWP were outlined: notably erosion/corrosion of heat exchanger shells due to by-passing seal; galvanic coupling with SS also resulted in excessive H₂ charging; delaminations of A516 Grade 70 plate as the result of the H₂ charging in the exchanger shell; large randomly oriented pits in the flare header due to deposition and a water level. Pitting was autocatalytic, increasing with time. Chlorides added to the pitting rate. Intergranular corrosion of sensitized material and transgranular cracking of cold-worked SS (SSCC) were noted.

84. M.G. Hay and D.P. Dautovich of Ontario Hydro Research, 'Characteristics of H₂ Damage at BHWP' - Presented to CIM Conference, Halifax, August 20, 1980
-

Hydrogen damage noted at the BHWP in absorber towers and rundown tanks was in the form of step-wise cracking also referred to as delamination, HIC or blistering. It was postulated that the following would give better performance - lowering the sulphur content, making cleaner, more homogeneous steels, using semi-killed steel, controlling the shape of the sulphide inclusions by Ca-Argon blowing - using Cu additions or cladding the steel. In addition, preconditioning to produce a sulphide layer could be utilized although it was found that films formed in moist H₂S gas allowed greater H₂ permeation than films formed in H₂S saturated liquid. However, in the presence of large amounts of oxygen, sulphide

layers were ineffective in reducing the permeation rates. But, when the oxygen was removed, both the gas-formed and liquid-formed sulphides were equally effective in reducing H₂ permeation.

Use of Cu was advocated but later studies have revealed its ineffectiveness at low pH.

85. R.J. Twigg, 'Corrosion of Materials in the Heavy Water Industry' - Presented to the CIM Conference in Halifax, August 26, 1980

Corrosion problems encountered in AECL heavy water plants tend to be delaminations or blisters, erosion/corrosion and pitting. Pitting is particularly active in areas of two-phase flow and low flow. Failures in the heavy water plants tend to be of the "weep" variety rather than by catastrophic cracking.

86. R.D. Kane of Cortest Laboratories Inc., Texas, 'The Roles of H₂S in the Behaviour of Engineering Alloys' - Presented at the CIM Conference - H₂S Symposium, Edmonton, Alberta, August 21-24, 1983

This basic instructional paper outlines the effects of H₂S environments on various materials. Sulphide stress cracking of low alloy steels is generally dependent upon pH, temperature and H₂S concentration. It increases with decreasing pH, decreasing temperature, and increasing H₂S concentration. SSC susceptibility is greatest at 21°C (70°F).

HIC is also dependent upon the same parameters, with greater susceptibility with low pH, decreasing temperature, and increasing H₂S concentration.

Cracking in pipelines is rather uncommon due to corrosion control programs using inhibitors and dehydration.

For high alloys, martensitic SS is more susceptible than other alloys and should be used in the quench-and-tempered condition.

Duplex alloys are susceptible to cracking in H₂S-containing brines and appear to be associated with cracking in the ferrite phase by hydrogen embrittlement.

Austenitic alloys generally are resistant unless cold worked or sensitized.

Nickel base alloys are highly resistant but embrittlement may occur associated with high temperature heat treatments between 260-538°C (500-1000°F).

87. D.L. Sponseller, R. Garber, and J.A. Straatmann of Climax Molybdenum, 'Effect of Microstructure on Sulphide Stress Cracking Resistance of High-Strength Casing Steels' - Presented at the CIM Conference H₂S Symposium, Edmonton, Alberta, August 21-24, 1983

Tests carried out on high-strength Cr-Mo and Mn-Mo casing steels reveal that a number of processing variables affect the SSC resistance of the alloys. SSC resistance is aided by refining the austenite grain size, by achieving a fully

martensitic microstructure during hardening, by increasing the tempering temperature, and by water quenching after tempering. The SSC resistance is degraded by tempering just above the ACl and then water quenching. Cast structures were found to be comparable to wrought structures in SSC resistance. However, the data presented seems to suggest that the castings were superior to the wrought products.

To provide martensitic structures, steels with high hardenability should be chosen.

Good SSC resistance is favoured by tempering martensitic structures at temperatures sufficiently high to produce rather coarse carbides in a relatively dislocation-free matrix. Too high a tempering temperature, however, decreases SSC resistance by forming untempered bainite or martensite.

Exposure of alloys prone to temper embrittlement will result in SSC degradation.

88. G.J. Bieffer and M.J. Fichera of Canmet, 'Sulphide Stress Cracking and Step-wise Cracking Tests on Gas Transmission Linepipes' - Presented at CIM Conference - H2S Symposium, Edmonton, Alberta, August 21-24, 1983
-

Testing was carried out on pipeline steels of Grade 290 and 483 to examine the material for resistance to SWC and SSC. It was generally concluded that in welded samples SSC was most prevalent in the HAZ, next, in the parent metal, with only slight damage to the weld fusion zone. SSC failures in parent metal occurred essentially by SWC. In both the SSC and SWC tests internal blister cracks, often linked by transverse cracks, were formed in the rolling plane suggesting that pipes resistant to SWC might also be resistant to SSC. Susceptibility to SWC increases with yield strength. There were indications that increased resistance to SSC could be correlated with decreased resistance to SWC. It had been thought that increased resistance to SSC correlated directly with increased resistance to HIC.

89. G.L. Derby of Shell Canada, 'The Use of Corrosion Inhibitors by the Oil and Gas Industry' - Presented at CIM Conference - H2S Symposium, Edmonton, Alberta, August 21-24, 1983
-

This very general paper discusses inhibition principals and program expectations.

90. Barry B. Wolt of Hanson Materials, 'Material and Service Related Failures Encountered in Sour Gas Environments' - Presented at CIM Conference - H2S Symposium, Edmonton, Alberta, August 21-24, 1983
-

Six case histories of failures of oil well tubulars and other drilling equipment were outlined. In every case, failure occurred in areas of the components possessing hardness above the recommended Rc 22. The high hardness stemmed from such things as poor or non-existent heat treatment, mechanical damage during straightening, and hard spots produced by local quenching during manufacture.

91. R.J. Twigg of Glencor Engineering Limited, 'Quality Assurance for Components in Hydrogen Sulphide Service' - Presented at the CIM Conference - H₂S Symposium, Edmonton, Alberta, August 21-24, 1983
-

A summary is given of methods of quality assurance that can and should be applied to components for sour service:

- (1) 100% U.T. scan with 25 mm circle rejection rate for laminations in plate.
- (2) Pilot heat treating of studs to ensure correct properties, rather than rely on ASTM A193-B7M because manufacturers tend not to temper properly.
- (3) Control of welding consumables with a proof test on each batch.

92. M.G. Hay of Shell Canada, 'An Electrochemical Device for Monitoring Hydrogen Diffusing Through Steel' - Presented at CIM Conference - H₂S Symposium, Edmonton, Alberta, August 21-24, 1983
-

This paper describes the various hydrogen monitoring probes that may be attached to pipes to detect H₂ passing through the wall. The Ontario Hydro-type probe, used in the Burnt Timber gas field, is described. The amount of H₂, lead to the determination that Co was insufficient to cause cracking.

93. S. Mukai, H. Okamoto, T. Kudo and A. Ikeda of Sumitomo, 'Corrosion Behaviour of 25% Cr Duplex Stainless Steel in CO₂-H₂S-Cl- Environments' Materials for Energy Systems, Volume 5, No. 1, June, 1983
-

It was shown that the corrosion resistance of the alloy increased with increasing Cr, Ni and Mo contents. SCC occurred when the Ni content was below 6% at high temperatures. Low temperature aging increased the susceptibility to SCC.

94. J.A. Straatmann and P.J. Grobner of Climax Molybdenum, 'High Strength H₂S Resistant Steels and Alloys for Oil Field Tubular Products' - from "Molybdenum Containing Steels for Gas and Oil Industry Applications - A State-of-the-Art Review" - Climax Molybdenum
-

Oil tubular goods were tested using a three-point loading and a double cantilever beam specimen in 0.5% acetic acid solution saturated with H₂S. pH was about 3.5. It was determined that quench-and-tempered martensite was the best structure for resistance to SSCC. Modification with Niobium raised the threshold level for SSCC.

95. R.S. Pathania of CRNL, 'Localized Corrosion of Stainless Steels and Nickel Alloys in Water Saturated with Hydrogen Sulphide' - Presented to NACE Eastern Region Conference, Montreal, September 27-29, 1977
-

Both austenitic and ferritic stainless steels were tested in environments simulating those that might be expected in heavy water plants. Martensitic, ferritic and austenitic type 304 and 347 stainless steels cracked in environments of H₂S, H₂O and 500 mg Cl-/Kg with and without oxygen. Type 316 stainless steel, on the other hand, cracked only in the presence of oxygen. Cracks often initiated at the bottom of pits. High nickel alloys, such as Inconel 625, Inconel X750, Incoloy 825, Hastelloys B, G and 276 and Ferralium, did not crack.

Cold-worked 316 and Inconel 625 did not crack in oxygen-free solutions. However, type 316, cold-worked, did crack in the presence of oxygen while Inconel 625 did not.

Cracking was encountered with 316 SS and 304, both heat-treated at 649-760°C. 321 failed after furnace cooling from 649°C. Cracking was intergranular. No cracking was found on the L grades or 347.

96. T. Kaneko, H. Kajimura and A. Ikeda of Sumitomo, 'Influence of Various Factors on the Uni-Axial Tension Load Test for Sulfide Stress Cracking' - Paper 161 - presented at NACE Corrosion 1983 - Anaheim, California, April 18-22, 1983
-

Tests conducted by dead weight loading of samples can give false readings of the initiation stress required for SSC. General corrosion reduces the sample size so that the applied stress becomes greater as the test progresses. Similarly, if pitting occurs, the stress concentration created can result in SSC when, in fact, the applied stress might not be high enough to cause cracking. The longer the test, the greater the possibility of error but long duration tests may be required to properly assess the effects on engineering alloys. Solvent volumes should also be examined as pipelines see a continuing flow of material and not just the same small volume-to-surface-area characteristic displayed in tests.

Many items often overlooked by other researchers are outlined. This is a good paper.

97. I.C.G. Ogle and W.G. Martin of Canmet, 'The Effects of Hydrogen on Pressure Vessel Materials Used in Heavy Water Plants' - Report ERP/PMRL 78-5 (IR) July, 1978
-

A literature survey and some testing of A516 Grade 70 tower plate from LHWP was carried out although much of the work was done on a G40.8 Grade B steel. The two materials are hardly comparable. It is concluded that Al203 provides a site for H₂ blistering. It also is concluded that embrittlement should not occur in the hot tower environments. The bulk hydrogen concentration found in A516 Grade 70 following a 21 day immersion at 30°C (duplicating a cold tower environment) was 1.0 ppm. It should be noted this is a lower level than other authors indicate is necessary to cause cracking.

98. M.G. Hay of Shell Canada, 'Hydrogen Induced Cracking - Resistant, Low Strength, Carbon Steel Plate for Hydrogen Sulphide Service' - NACE Western Canada, Conference, Calgary, February, 1983
-

Work performed on steels for the BHWP is outlined. It was found that cracking can occur when hydrogen flux Co reaches 6^Mg/g but not a lower level. Electroslag remelting results in a steel very resistant to HIC even though MnS inclusions are not shape controlled. The inclusions tended to be few in number, small and well dispersed. Alternatively, low sulphur of less than 0.005% and shape controlled with calcium, also resulted in material highly resistant to HIC. It is highly desirable to normalize or to quench and temper after rolling.

Shape controlling with rare earth metal additions was ineffective. Calcium treated, microalloyed, copper-bearing linepipe steels were found to have higher corrosion rates in moist H₂S gas environments than other steels.

99. H.R. Copson, 'The Influence of Corrosion on the Cracking of Pressure Vessels' - Reprinted from "The Welding Journal", February, 1953 Supplement
-

A short section in the paper refers to sulphur, arsenic, selenium, tellurium, antimony and phosphorus as components that promote the absorption of H₂ into steel. H₂S can produce iron sulphide to protect the steel, but in low pH solutions or in the presence of cyanide, the sulphide dissolves and H₂ penetration is promoted.

- 100 A. Ikeda of Sumitomo, 'Effect of Side Coating and Size of Specimen on HIC Test Result' - Presented to NACE T-1F-20 Task Group Meeting, Toronto, April 8, 1981
-

It was determined that side coating of specimens was desirable to simulate gas pipelines that receive hydrogen charging from only one side. In addition, the ratio of the width/thickness of the specimen can have a profound effect upon HIC resistance. It was recommended that the width/thickness ratio should exceed 4.

- 101 R.L. Tapping, P.A. Lavoie and R.D. Davidson of CRNL, 'Effect of H₂S Neutralization Methods on Sulfide Films in Heavy Water Plants' - Paper 103 presented to NACE Corrosion 1983, Anaheim California, April 18-22, 1983
-

The GS heavy water plants depend, to a large extent, on the presence of stable sulphide scales on the walls of pressure vessels and equipment to prevent excessive corrosion. When equipment is opened for repairs or inspection, the acidic environment is neutralized with ammonia or a carbonate wash. Experiments were conducted on synthetically produced scales to determine whether or not degradation of the scales occurred. It was concluded that neutralization methods did not destroy the protectiveness of the films. However, it was noted that upon re-exposure of neutralized coupons to the H₂S environment, an initial high rate of corrosion was experienced; this quickly reduced to normal rates. In addition blistering between scale layers was found, presumably between the old scale and that being newly established. Steaming and moist air exposure appeared to be more damaging to the films than neutralization. The protective films do lose some of their protectiveness when exposed to oxidizing conditions. No time span for exposure to oxidizing condition was studied.

- 102 R.S. Pathania, 'Stress Corrosion Cracking of Stainless Steels and Nickel Alloys in Water Saturated with Hydrogen Sulphide' - Proceedings of 8th International Congress on Metallic Corrosion, Mainz, FRG, Sept. 6-11, 1981
-

Essentially the paper is an update of that listed above (Ref. 95). It was determined that SSC of the alloys is affected by alloy composition, cold work and the presence of oxygen. Martensitic and ferritic alloys had poor resistance, austenitic alloys moderate resistance, and nickel-base alloys and titanium had excellent resistance to SSC. Cold working resulted in cracking of

austenitic alloys that had been resistant before, e.g. 316. Alloys such as 304 cracked in the absence of oxygen but higher alloys required oxygen in the solution to cause cracking.

103 D.R. Morris, L.P. Sampaleanu and D.N. Veysey of University of New Brunswick, 'The Corrosion of Steel by Aqueous Solutions of Hydrogen Sulphide' - "J. Electrochem Society", Volume 127, (1980)

This paper is often quoted as describing corrosion occurring in the GS process for the production of heavy water. However, the authors studied corrosion on 1020 steel in deaerated aqueous solutions at 25-30°C. Consequently, they were duplicating only some GS process conditions. The paper is quite theoretical and attempts to develop several formulae for various corrosion and weight-loss mechanisms. Basically they determine that:

- (a) H₂S makes the corrosion potential of 1020 steel more negative.
- (b) The corrosion current is dependent upon the H₂S concentration, increasing with H₂S concentration in the pH ranges studied.
- (c) The corrosion product generated, mackinawite, is not adherent, particularly at velocities exceeding 2 m/sec.
- (d) Mackinawite may, under certain circumstances, increase the corrosion rate of the underlying steel, particularly in the presence of NaCl. (Limiting velocities must be applied to equipment design.) An incubation period prior to the onset of corrosion was noted.

An increase in corrosion rate was found with time and velocity.

Although some important points were noted, it is dangerous to equate this paper with corrosion environments of the heavy water plants. For instance, 1020 steel would not be used in the pressure envelope.

104 David W. Shoesmith, Peter Taylor, M. Grant Bailey, and Derrek G. Owen of AECL Whiteshell, 'The Formation of Ferrous Monosulphide Polymorphs During the Corrosion of Iron by Aqueous Hydrogen Sulphide at 21°C', "J. Electrochem Society", Volume 127, (1980)

The authors studied the formation of sulphide films on iron in unstirred, saturated, aqueous solutions of H₂S at 21°C and at atmospheric pressure. They found mackinawite formed, cracked off, and then formed again as a pitted and cracked layer. Cubic ferrous sulphide and, lastly, troilite formed. The rate of corrosion increased with decreasing pH. Below pH3 the precipitated scales tend to dissolve. Significant passivation was found only at pH7 where the mackinawite layer remained intact.

105 D.R. Bell, R.B. Casault and J.D. Boyd of Canmet, 'A Metallurgical Evaluation of Grade 483 Line Pipe', "CIM Bulletin", Volume 75, No. 841, May, 1982

Sections of pipe from commercial runs of longitudinal weld and from spiral weld pipe were tested for consistency of response to tests. It was determined that

the Charpy tests at the 1/4 width location should probably be moved to the 1/2 width location to test the worst material.

This is an interesting report although not directly applicable to sour gas conditions.

- 106 P.R. Rhodes, G.A. Welch and L. Abrego of Shell Development, 'Stress Corrosion Cracking Susceptibility of Duplex Stainless Steels in Sour Gas Environments', "Journal of Materials for Energy Systems", Volume 5, No. 1, June, 1983
-

Stress corrosion cracking (SSC) susceptibility of duplex stainless steel tubulars in oxidant-free NaCl/H₂S solutions simulating downhole sour gas well environments, was evaluated using a number of alloys of 21-25% Cr -5% Ni and 3% Mo in both the annealed and cold reduced conditions. Transgranular cracking of all alloys was observed. Anodic rather than cathodic test conditions accelerated the SSC, indicating that the cracking was promoted by corrosion rather than H₂ charging. Cracking occurred in both the ferrite and austenite phase although grain boundary cracking between the phases also occurred. Heavy selective corrosion of the ferrite phase was observed.

Specimens, not anodically charged nor containing previously formed pits, did not corrode nor stress crack.

The acidity of the solution is important as there is a greater tendency in highly acidic solutions toward general corrosion, from which SSC can develop. Similarly, in very acidic solutions cathodic activation can cause SSC.

The investigation suggested that absorbed H₂ had little to do with producing SSC.

Increasing H₂S partial pressure and Cl⁻ levels increase cracking tendencies. In addition, raising the temperature results in increased cracking up to 150°C, probably due to increased pitting. Above 150°C, improved resistance to SSC results.

Presence of O₂ increased the pitting corrosion tendency.

- 107 A.P. Coldren and G. Tither, 'Metallographic Study of Hydrogen Induced Cracking in Line Pipe Steels', "Journal of Metals", Volume 28, No. 5, May, 1976
-

Bainite and martensite promote cracking in high strength steels in sour environments. Microscopic studies of high-strength low-alloy line pipe (X65) (one, a Cb-V steel and the other, a Mo-Cb steel) revealed that isolated islands of bainite and martensite had no effect on the HIC of the materials. Cracking was always associated with inclusions. The inclusions tended to be rare earth sulphides with an aluminum phase, probably alumina. It was postulated that the rare earth sulphides tended to remain attached to the fracture surfaces and so could be readily identified.

As the % of martensite in the alloys was less than the generally accepted 30 required for SSC, HIC cracking is obviously a different phenomenon. Hence, controlling Cr, Mn, and Mo in low alloy steels will not reduce the risk of HIC.

Some method must be found to reduce the inclusions or to prevent H₂ entry into the steel.

- 108 Hideya Okada of Nippon Steel Corporation, 'Stress Corrosion Cracking and Hydrogen Cracking of Structural Steels' - Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys - Proceedings of NACE 5 Conference, Jniseux-Firming, France, June 12-16, 1973
-

A portion of the paper refers to SSC of liquid PG storage tanks due to H₂S in natural gas. The presence of 1% Ni was found to decrease the amount of H₂ necessary to cause cracking (i.e. 10 ppm without Ni and 4 ppm with it, to cause cracking). Failures were in the HAZ. It was concluded that no cracking occurs without water no matter what the H₂S level. H₂S concentration must be above 100 ppm for cracks to form.

In addition, it is shown that a steel's resistance to HIC can be increased dramatically by lowering the S content.

- 109 R.R. Fessler, T.P. Groeneveld and A.R. Elsea of Battelle, 'Stress Corrosion and Hydrogen Stress Cracking in Buried Pipelines' - Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys - Proceedings of NACE 5 Conference, June 12-16, 1973
-

The authors refer to Hydrogen Stress Cracking of pipeline steels in which failure occurs as a single, clean, relatively flat fracture surface with no branching cracks. Where short branches were observed, they followed the prior austenite grain boundaries. These failures tended to occur at hard spots in the pipe or HAZ. Hard spots have been found to contain 100% martensite. All failures reported by the authors occurred in coated and cathodically protected pipe. Source of H₂ was thought to be the cathodic protection.

One-side charging should be used in experiments to simulate the pipeline.

- 110 E.C. Greco and J.B. Sardisco, 'Reaction Mechanisms of Iron and Steel in Hydrogen Sulfide' - Proceedings of the Third International Congress on Metallic Corrosion, Moscow, 1966
-

The authors studied hydrogen penetration of steel with the hydrogen generated by corrosion. They found that sulphide films forming on the metal were protective if pyrite was formed. Kansite (Mackinawite) proved to be non-protective. Films were non-protective at pH 6.5 to 8.8. The rate of H₂ penetration was related to the density of the scale. In addition, it was concluded the hydrogen penetration rate depended on the concentration of the corroding species and the metallurgical structure, i.e. pearlite absorbed three times as much H₂ as martensite at the same H₂S concentration, even though the amount of corrosion was the same.

- 111 Eihachiro Sunani, Masayuki Tanimura, and Gennosuke Tenmyo, 'Stress Corrosion Cracking of Pipeline Steels' - Proceedings of 5th International Conference on Corrosion, Tokyo, Japan, 1972, NACE Publication
-

Experiments were conducted on line-pipe steels in a NACE solution with hydrogen

charging as might be found in cathodic protection. Both Sulphide Stress Cracking and Hydrogen Stress Cracking were investigated. In low-strength steels both effects appear identical with the formation of internal blisters linked by tearing. In higher strength steels, failure was associated with the microstructure.

The cracks in the quenched and tempered alloys followed prior austenite grain boundaries. In the as-rolled samples, cracks connected blisters. The blisters had formed parallel to the rolling direction.

It was concluded that pipelines up to X100 are not susceptible to delayed failures due to H₂ sulfide stress corrosion, or to hydrogen charging from cathodic protection.

112 Y. Nakai, H. Kurahashi, N. Totsuka, Y. Wesugi and I. Kawasaki-cho of Kawasaki, 'Effect of Corrosion Environment on Hydrogen Induced Cracking' - Paper 132, NACE Corrosion 1982, Houston, March 22-26, 1982

H₂S contamination of natural gas pipelines under wet conditions produces HIC in steels. The authors investigated several steels. After exposing one side of the samples to H₂S containing solutions, they measured the current generated by the hydrogen passing through the steel. It was determined that the permeation rate increases with increased H₂S content, and with decreasing pH. Cu added to steel decreases the permeation rate if H₂S concentration is less than 1500 ppm. Above this level the permeation rate increases dramatically. Cu is effective only under mild pH conditions. The threshold hydrogen permeation rate required to generate HIC is about 6 MA/cm² for both low S steels and Cu treated steel. The critical partial pressure of H₂S in sour gas required to generate HIC is 0.2 atm for low S steel, 0.6 atm for Cu steel and over 15 atm for Ca treated steel.

113 F.W. Hewes, 'Monitoring Internal Corrosion in Pipelines Transporting Natural Gas Containing CO₂ and H₂S' - Proceedings of the 5th International Conference on Corrosion, Japan, 1972

A corrosion monitoring program using corrosion coupons, electric resistance probes, hydrogen probes and removable test spools was tested both in the laboratory and in the field. It was determined that hydrogen probes, provided that they were carefully pretested and calibrated for internal volume, exposed probe shell area, and changes in probe temperature, yielded the best on-stream results, closely followed by removable corrosion spools and coupons. Long term corrosion rates were found to be easily predicted from short term corrosion spool tests provided there was a tendency for adherent, partially protective, scales to form.

Electric resistance probes proved to be disappointing as reproducibility of tests results was questionable. Polarization Resistance Probes were useful, of course, only where continuous electrolyte was present.

It was determined that corrosion monitoring should take place in areas of high turbulence, in stagnant areas, and in liquid phases.

Each stream and process leg should be monitored due to variation in corrosivity.

It was determined in service, that an Hydrogen Transmission Rate of 1 mml/cm²/day should be cause for alarm as blistering and cracking were likely.

- 114 N. Seki, T. Kotera, T. Nakasawa, Y. Kobayashi, T. Taira of Nippon Kokan, 'The Evaluation of Environmental Conditions and the Performance of Linepipe Steels Under Wet Sour Gas' - Paper 131, NACE Corrosion 1982, Houston, March 22-26, 1982
-

Hydrogen permeation tests and pH value measurements were carried out in synthetic sea water, and in pure water, with pressurized H₂S and carbon dioxide. It was determined that hydrogen pressure, as measured by a patch probe, builds quickly in the early stages and then gradually becomes less - probably indicating production of a scale. Hydrogen permeation rates increase with increasing H₂S and are accelerated by the addition of carbon dioxide. Corrosion rates were said to depend upon the pH and it was felt that the severity of sour gas in a pipeline can be determined by monitoring the H₂ passing through the wall.

- 115 T. Taira, Y. Kobayashi, K. Ume, T. Hyodo, N. Seki, T. Nakazawa of Nippon Kokan, 'Study of the Evaluation of Environmental Conditions of Wet Sour Gas' - Paper 156 NACE Corrosion 1983, Anaheim, California, April 18-22, 1983
-

Six types of line pipe were examined in synthetic sea water, the NACE solution and de-ionized water (all saturated with H₂S). Two steels had low temperature transformation structures at their centres and high amounts of MnS. These steels were the most susceptible to cracking. Two steels were Cu-bearing and showed improved HIC resistance. However, the effect of the Cu was not always beneficial and was found to depend upon the gas composition. Two steels were very clean and contained little or no segregation bands. These steels proved the best in HIC resistance.

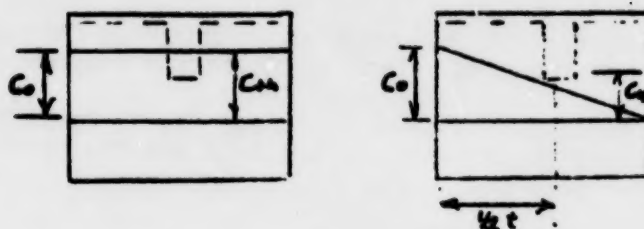
Testing was done from one side and from all sides.

Corrosion products tended to suppress the corrosion rate but their effect was not always constant and depended upon pH. Lower pH tended to result in no protective films.

Hydrogen permeation tended to occur some hours after immersion and reached its maximum rate around 40 hours. Dramatic decreases were experienced in some alloys and test conditions as scales formed. In deionized water, the decreases were gradual.

HIC was most prevalent with all side charging and crack lengths tended to be less under one side charging.

It became clear that there was a critical permeation rate below which HIC would not occur. This critical permeation rate depended upon material microstructure and gas compositions. In one side charging, hydrogen passing through the steel would bleed off, resulting in lower H₂ contents and hence, reduced HIC.



The hydrogen permeation rate could be used as a measure of a steel's resistance to HIC provided protective scales do not form. Susceptibility to HIC is dependent upon the test method.

This paper continues to develop the critical hydrogen concentration theory proposed by the Japanese as necessary to cause cracking.

116 M. Hill, E.P. Kawasaki and G.E. Kronbach of Republic Steel, 'Oil Well Casing: Evidence of the Sensitivity to Rapid Failure in an H₂S Environment', "Materials Protection and Performance", Volume 11, No.1, January, 1972

This paper outlines early attempts to determine the effects of microstructure on the cracking resistance of steels in H₂S solutions. The authors suggest that hardness or ultimate tensile strength alone does not adequately describe the resistance of a steel to aqueous hydrogen sulphide. They tested steels to API N-80 and P-110 grades, heat treated to various conditions. Most of the steels contained significant amounts of copper but tests were carried out at pH's below which copper should have been effective in reducing hydrogen permeation. It was found that structures that were quenched to uniform martensite without the retention of austenite and then tempered, had the best resistance to sulphide attack. Steels of equal hardness levels do not necessarily have the same sulphide cracking resistance. Microstructure governs the response.

Microstructure has long been suggested as the governing aspect of cracking and this paper was one of the first to say so.

117 M. Watkins and E.L. Van Rosenberg of Exxon Research, 'Sulfide Stress Cracking Resistance of Weld Repairs in Wellhead Alloys' - Paper 159 presented at NACE Corrosion 1983, Anaheim, California, April 18-22, 1983

Two cast alloys A487-9Q and CA-15 (12% Cr) commonly used in wellhead castings were weld repaired and evaluated for resistance to SSC. The SSC resistance of weld repairs in the as-welded condition was grossly inferior to that of the unrepaired casting. Poor SSC resistance was attributed to high hardness in the heat-affected zone. Normal stress-relieving temperatures of 593°C (1100°F) only marginally reduced the hardness and improved SSC resistance. Higher temperature of 649°C (1200°F) and 704°C (1300°F) produced significant reductions in hardness

and improvements in SSC resistance. The microstructure in the heat-affected zone of the weld repair, even when stress relieved, was more susceptible to SSC than the base metal in a non-repaired component. Microstructures in the heat-affected zones of as-welded material tended to be modestly tempered martensite.

- 118 Gerdt Wilken of Mobil Oil, West Germany 'Some Results in Combatting H₂S Corrosion in Sour Gas Operations' - Paper 158 presented at NACE Corrosion 1983 Anaheim, California, April 18-22, 1983
-

Experiments indicate that the structure of steel has an influence on the corrosion of steels. Reducing the S, Ni, and Cr content of the steels, lowers the corrosion rate. HIC cracking occurs in the segregation bands. Ultrasonic inspection using straight and angled probes is used to detect damage in a 100% scan of susceptible material. Blisters were found to initiate at MnS inclusions or at Al₂O₃ clusters where the Ni content was found to be somewhat higher.

- 119 A. Brown and C.L. Jones of British Gas Corporation, 'Hydrogen Induced Cracking in Pipeline Steels' - Paper 155 presented at NACE Corrosion 1983, Anaheim, California, April 18-22, 1983
-

Studies of HIC in BP and NACE test conditions were undertaken to assess a number of variables. It was concluded that non-metallic inclusions, primarily MnS but also clouds of alumina particles, were the primary initiation sites for HIC. Elongated sulphides, particularly in the mid-wall position where there was a high degree of banding of pearlite and of martensite/bainite, were much more likely to initiate cracking than were round sulphides. Lowering the sulphur content to less than 0.005% could be effective in reducing HIC. Fully-killed steels tend to be more susceptible to HIC than semi-killed due to segregation and to the presence of alumina as well as of elongated sulphides. Calcium-treated steels all show a lower susceptibility to HIC due to MnS shape control. Quenched and tempered steels and normalized steels were more resistant to HIC than controlled rolled steels.

Small additions of copper, nickel and/or chromium can improve HIC resistance of pipeline steels under the mild BP test conditions.

- 120 D.A. Hansen, and E.M. Moore Jr., 'Materials Selection for Sour Wet Service', - Second Middle East Corrosion Conference, Bahrain, January 19-21, 1981
-

A brief outline is given of some materials used in wet sour service. Sections of MR-01-75 are utilized. In general, velocities should be limited to 3 m/sec (10 ft/sec) in liquid service, to 22.5 m/sec (75 ft/sec) with carbon steel coated with fusion bonded material, to 15 m/sec (50 ft/sec) with cold cured coatings and to 22.5 m/sec (75 ft/sec) with austenitic stainless steel. Carbon steel vessels are specified as A516 - no grade given. Weld and HAZ hardness must be less than RC 20. Seamless C.S. pipe is used for diameters less than, or equal to, 40 cm (16") and double submerged arc welded longitudinal seam pipe for diameters over 40 cm (16"). Spiral weld pipe may be used only if pipe is internally coated. Valves use austenitic 316L with Inconel 825, 625, etc. Stems are of various high alloys.

121 B.A. Gordon, W.D. Grimes and R.S. Treseder of Shell, 'Casing Corrosion in the South Bebridge Field' - Paper 157 Presented at NACE Corrosion 1983 Anaheim, California, April 18-22, 1983

Corrosion discussed in this paper was not caused by a sour environment.

122 Jan Oredsson and Sven Bernhardson, Sandvik, Sweden, 'The Performance of High Alloyed Austenitic and Duplex Stainless Steels in Sour Gas and Oil Environments' - Paper 126 presented at NACE Corrosion 1982, Houston, Mar 22-26, '82

A duplex alloy and a high-nickel, austenitic alloy were tested in the NACE solution and in simulated downhole environments. It was determined that cold working increased the duplex alloy's tendency to crack. In addition, it was suggested that pH was more critical than H₂S content in determining cracking resistance. The lower the pH, the greater the tendency to crack. The chloride content was also found to have a great influence on the cracking resistance, due to pitting attack.

123 P.W. Rice, R.A. Beverly, C.E. Ivey, and B.R. Keeney, 'New Alloys for Oil and Gas Hydrogen Sulfide Service', "Materials Protection and Performance", Volume 12, No. 10, October 1973

Laboratory and field tests were conducted on C-ring test specimens of various alloys, examining their resistance to SSC and general corrosion. The alloys were required to provide resistance to sulphide stress cracking under the following conditions:

- (a) 0.2% offset yield stress,
- (b) 13.6 J (10 ft/lbs) minimum and 20.3 J (15 ft/lb) average full size transverse Charpy V impact strength at -57°C (-70°F) and
- (c) minimum 0.2% offset tensile yield stress of 414 MPa (60,000 psi).

Successful Alloys Were:

- (1) AISI 4340 (Quench and Temper, 26 Rc)
- (2) Vulcan Steel Astralloy (Quench and Temper, 25 Rc)
- (3) Inco K-Monel (Mill Annealed and Age Hardened 29 Rc)
- (4) A-286 (Solution annealed 982°C (1800°F) and Aged 718°C (1325°F), mill treated to 32 Rc).
- (5) Titanium Alloy 6 Al-4V (Mill Annealed, 33 Rc)
- (6) J+L 304N, (cold worked by Mill to Rc 26)
- (7) Armco PH 13-8 Mo (Supplied by Mill in annealed condition, heat treated to condition H 1150 M, 30 Rc).

Alloys not meeting test requirements included Armco 15-16 WR, Uniloy-326, E-Brite 26-1, Vaculoy 26-1, Armco 18-2 Mn, Armco 22-13-5, Custom 455 and Custom 450.

124 M.H. Bartz and C.E. Rawlins of Phillips Petroleum, 'Effects of Hydrogen Generated by Corrosion of Steel', "Corrosion", Volume 4, No. 5, May, 1948 (Classic Paper)

This paper outlines case histories and tests performed on materials from Natural

Gas Plants, Oil Refineries and Process Piping from the Phillips group of companies.

Embrittling and blistering were encountered in equipment handling sour crude, sour crude fractions, sour natural gases and gasolines. (Ed. comment - natural gasolines refer to the hydrocarbon liquids found in many natural gas wells.) Blisters varied in size from 3 mm up to 300 mm x 600 mm (1/8" up 12" x 24"). The number of blisters varied from plate to plate. They were frequently encountered in bands in the steel and were generally parallel to the rolling direction. A survey of natural gas plants revealed that five out of the ten carrying sour products, had suffered varying degrees of blistering; no plants handling sweet crudes had suffered blistering. Only one case of a blistered pipe was encountered but the history was lost.

Blisters were drilled and the gas analyzed. It was found to be 99.5% H₂. Sometimes sparks from an electric drill ignited the gas causing violent explosions. Five blisters that developed in a refinery vessel were tapped and the gas pressure measured. Values of 6.89, 11.7, 17.2 and 19.6 MPa (1000, 1700, 2500 and 2700 psi) were recorded. The maximum operating pressure in the vessel was 1.86 MPa (270 psi), and 2.8 MPa (405 psi) during hydrostatic testing.

A natural gasoline vessel that had been removed from service and then filled with gas at 206 KPa (30 psi) ruptured. The vessel failed along the knuckle radius of one head. Blisters along this knuckle radius had torn open to form a discontinuous chain of cracks along the failure line. Blisters tended to be parallel to the rolling direction.

Blisters bulged both to the inside and outside surfaces. Cracks were frequently found at blister edges, at right angles to the original blister direction (start of step-wise cracking).

Impact tests showed fibrous results and it was postulated that segregation of phosphorous had occurred and the blistering was concentrating in this segregation band. Large inclusions or small stringers of inclusions were also considered as prime areas for blister formation. It was also felt that many of the blisters occurred at plate laminations that had not been closed by rolling. This conclusion is now considered unlikely.

Vessels in service were found to have blisters that had ruptured to the inside, producing long cracks running from the blister edges to almost half the shell thickness. This suggests SSC originating from blisters.

A blistered pressure vessel was tested to destruction to determine whether or not embrittlement had occurred. The vessel was 600 mm (24") in diameter x 2.25m (7.5 ft) long with a shell thickness of 4.7 mm (3/16") and had been used as a make-up tank water leg in a sour natural gasoline plant. It contained numerous, closely spaced blisters up to 50 mm (2") in length.

Under test the vessel leaked at a 11 mm (7/16") crack at the edge of a blister. The yield point had been exceeded only slightly as the increase in circumference was only 0.3%. The hoop stress at bursting was 268 MPa (35,800 psi)

versus 310 MPa (45,000 psi) for an undamaged section, indicative of a reduction in wall thickness of 22%. No embrittlement was detected.

The paper recommended the use of fully-killed steels of better quality to control H₂ damage. We know now that these steels are not adequate.

Repair of blisters frequently involved venting, gouging out the blister and filling the void with weld metal.

Embrittlement was controlled in sucker rods years ago by operators pouring hot oil over the embrittled component. This, of course, resulted in H₂ diffusing out of the structure, reducing its brittle characteristics.

125 Working Within Metallurgical Limitations in the Successful Repair Welding of Power Plant Components by W.H.S. Lawson and D. Mills - Ontario Hydro Research - Presented at CIM - 19th Annual Conference of Metallurgists, Halifax August 25, 1980

Studies were carried out on "Temper Bead" welding for repairs to power plant components as allowed by ASME Code for the repair of nuclear power plant components. The technique involves strict control of the heat input, bead size and deposition location in an attempt to refine the heat-affected zone of underlying beads using the heat from upper ones to prevent hard spots. The authors contradict themselves somewhat by indicating that the highest hardness found at the toe of the welds just meets or even exceeds the maximum required for components for sour service even under the most controlled procedure. Tests in sour solutions, however, showed no cracking. Lower preheat temperatures have been used for power plant components, presumably producing harder heat-affected zones. Still, these components are to be used in relatively high temperature service where some stress relief might occur in the long run.

Temper Bead Welding does not remove residual stresses and this can lead to failure under low temperature or stress corrosion environments. In addition, resistance to sulphide cracking depends upon extremely close control over the technique. Sloppiness could easily lead to failure.

In this study hardnesses of heat-affected zones have all been measured on a macroscopic basis while it is generally recognized that microcracks formed in small hard zones can easily propagate, causing failure.

126 Badrii S. Jassem of Daura Refinery, Bagdad, Iraq, 'Case Histories of Refinery Corrosion', "Anticorrosion Methods and Materials", Volume 26, No. 3, March, 1979

This paper outlines five cases of corrosion.

In one an overhead drum suffered hydrogen blistering and pitting due to 2.0 - 4.2 mole % H₂S in the streams. Temperature was about 37.8°C (100°F) with pressure of 68.9 KPa (10 psi). The vessel was lined with Monel. The injection of a filming inhibitor and a neutralizing inhibitor were used to control the attack.

- 127 T.V. Venkatasubramanian and T.J. Baker, 'Role of Elongated MnS Inclusions in Hydrogen Embrittlement of High-Strength Steels', "Metal Science", Volume 16, No. 12, December, 1982
-

The role of elongated non-metallic inclusions in hydrogen-assisted cracking was studied as a function of yield strength, hydrogen activity, inclusion orientation and volume fraction, using two medium-strength steels. Crack velocities were greatest in the short transverse orientation and smallest in the longitudinal orientation. Increasing the volume fraction of inclusions increased the threshold stress necessary for cracking in the longitudinal direction but decreased it in the transverse direction. Increasing the hydrogen activity by increasing the H₂S concentration resulted in greater susceptibility to cracking. The presence of elongated sulphides in the short transverse direction resulted in strain intensification, reducing the stresses required to initiate cracking. In the longitudinal direction, triaxial stresses were reduced, raising the stress necessary to initiate fracture.

It was demonstrated that crack-growth rate is related to hydrogen diffusivity and, if the hydrogen concentration ahead of the crack tip reaches a critical level, cracking results. These authors conclude that inclusion orientation has no effect on diffusivity, hence cracking is anisotropic. Other studies conclude that orientation has a great deal of effect on diffusivity as long thin inclusions, with the long direction at right angles to the diffusion path, capture more hydrogen than those with the small dimension at right angles to the flow. Consequently, crack damage is more likely and more hydrogen will diffuse to the site due to the stress-assisted mode.

- 128 Friedrich Karl Naumann, 'Failure Examination, Corrosion by Hydrogen Sulphide - Corroded Pipes from Gas Generating Plant', "Praktische Metallographie", Volume 13, No. 12, 1976
-

This study involves a high temperature, not a sour gas environment.

- 129 A. Ikeda, T. Kaneko and F. Terasaki of Sumitomo, 'Influence of Environmental Conditions and Metallurgical Factors on HIC Initiation on Line Pipe Steel in Wet H₂S Environment' - Proceeding of Second JIM International Symposium, Hydrogen in Metals, November 26-29, 1979 - published Japan, 1980,
-

Experiments determined that two factors - C_{th} which is the threshold level of H₂ to cause HIC, and C_o which is the amount of H₂ absorbed from the environment - must be considered. If C_o is greater than C_{th}, cracking results. The addition of Cobalt to the alloy in amounts over 1% will significantly reduce C_o. In addition, Cobalt plus copper additions can effectively reduce C_o in solutions of pH 3-3.5 and prevent cracking.

It is assumed that a stable scale is formed. Cu additions can reduce C_o in solutions with pH 4.0 and eliminate HIC in solutions with pH 5.0.

C_o and C_{th} concepts were advanced many years ago by Troiano but tended to be ignored until revised by this and other papers published about the same time.

- 130 T. Kukuzuka, K. Shimogori, Y. Torii and K. Kitahata, 'Effect of Nitride in Steel on Hydrogen Induced Cracking of Line Pipe Steels' - Proceeding of Second JIM International Symposium, Hydrogen in Metals, November 26-29, 1979 - published Japan, 1980
-

Experiments were conducted to study metallurgical factors in Hydrogen Induced Cracking of pipeline steels, API X60-X70, in wet H₂S environments. It was determined that elongated sulphides had the most effect on Hydrogen Induced Cracking. Copper in the steels was effective in reducing HIC, but, pH was not discussed. Dissolved nitrogen was found to be very significant in reducing HIC. The dissolved nitrogen did not change the corrosion rate of the solutions but rather seemed to affect the rate of hydrogen diffusivity. It was postulated that nitrogen acted as a trap for the atomic hydrogen, reducing the diffusable amount so that the concentration required for cracking was not reached.

Dissolved N₂ also was found to reduce SSC in welds.

- 131 M. Sino, N. Nomura, H. Takezawa and H. Gondoh, Nippon Kokkan, 'Some Considerations on Prevention of Blister - Induced Cracking of Linepipe Steels in Hydrogenerating Environments' - Proceeding of Second JIM International Symposium, Hydrogen in Metals, November 26-29, 1979 - published Japan, 1980
-

Experiments performed for other papers are summarized in this one. It is shown that lowering the sulphur content of the steel drastically increases the resistance to blister cracking. This effect is related to both the decrease in number of MnS inclusions and also to a decrease in the absorption of hydrogen. (S equals 0.001%) Therefore, it is expected that the total volume of sulphide, its composition and shape, will control the steel's resistance to failure. Treatment with Ti and rare earth metals produce globular sulphides, reducing HIC tendencies.

External stress enhances the hydrogen volume for specimens containing more than 0.001% S. External stress tends to promote fracture by linking blisters in a stacked array perpendicular to the stress direction. The absence of stress results in step-wise cracking.

A pronounced shear stress peak at the crack tip produced by internal hydrogen pressure, is reduced by external stress applied parallel to the crack plane. This shear stress is considered to play an important role in nucleating second blister cracks by acting on manganese sulphide-matrix interfaces to trigger opening and to accelerate hydrogen precipitation there. Positions of stress high enough to form cracks will be located at blister crack tips in a step-wise direction if no external stress exists; with external stress, points of stress are found at the flank of the blister, a fair distance away from both tips. The authors conclude that Ni additions greater than 1% can substantially reduce the amount of absorbed hydrogen in solutions with a pH of 3-5, while Cu loses its effect in solutions with lower pH.

- 132 N. Taniguchi, S. Yanagimoto, T. Ishiguro and J. Kobayashi of Nippon - Kokan, 'Hydrogen Embrittlement of Steels in Saturated H₂S Solution Under Slow Extension Rate' - Proceedings of the 2nd JIM International Symposium, Hydrogen in Metals, November 26-29, 1979, published Japan, 1980
-

A new test has been developed to rate a steel's susceptibility to hydrogen embrittlement by determining the ratio, under slow strain rate conditions, in the solution versus in air.

- 133 Y. Nakai, H. Kurahashi, T. Emi and O. Haida of Kawasaki, 'Development of Steels Resistant to Hydrogen Induced Cracking in Wet Hydrogen Sulfide Environment', "Transactions of the Iron and Steel Institute of Japan", Volume 19, No. 7, July, 1979
-

Extensive tests were conducted on steels in the BP Solution to assess resistance to HIC, and methods of preventing it. It was determined that HIC is most frequently observed in areas corresponding to segregation in the ingots (either centreline or edge segregation). Crack propagation was shown to be along pearlite bands or in the bainitic or martensitic structure found in the Mn and P segregation areas. In fact, high levels of both Mn and P were detected around the cracks and in the cracks themselves. By decreasing the sulphur content of the plate, cracking in segregation zones can be reduced but not eliminated. Cu additions can reduce the rate of hydrogen permeation but not eliminate it. Heat treatment can be used to improve the solute segregation in the slabs, reducing susceptibility to HIC; this is considered impractical on a commercial scale. Semi-killed steels showed better resistance to HIC than Al fully-killed steels because sulphides tended to remain ellipsoidal. Shape control with rare earth metal additions or calcium was found to be extremely effective in preventing HIC even in controlled-rolled products.

Ultrasonic C-Scan studies were able to identify HIC. This method could be applied continuously throughout the experiment with one-sided charging. It was determined that a steel displaying a crack ratio of less than 20% by C-Scan had a cracking sensitivity of 0 and was unlikely to experience failure in service.

Crack Sensitivity Ratio = $\frac{\text{total step-wise cracking area } (\sum a_i b_i)}{\text{cross sectional area of sectioned coupon}} \times 100$

- 134 E. Miyoshi, T. Tanaka, F. Terasaki and A. Ikeda of Sumitomo, 'Hydrogen Induced Cracking of Steels Under Wet Hydrogen Sulfide Environment', "Transactions of the ASME Journal of Engineering for Industry", Volume 98, No. 4, November, 1976
-

Experiments carried out in the BP type solutions revealed that hydrogen-induced cracking originated at elongated MnS inclusions located in zones corresponding with segregation areas of the ingot. The hydrogen-induced cracking susceptibility decreased with decreasing sulphur content. Controlled rolling had little effect on low sulphur steels, but increased susceptibility to cracking in regular grades. Small amounts of copper were found effective in reducing HIC, due to the decrease in the amount of hydrogen absorbed. Residual strain in plate was found to decrease HIC susceptibility up to 10% strain. Above 10%, susceptibility is increased. Calcium or rare earth additions result in shape control of inclusions, thereby reducing susceptibility to cracking. (Pre-straining, however, can result in excessive cold work and accelerated failure by SSC.)

- 135 Z. Szcarska-Smialowska, E. Lunarska of the Polish Academy of Sciences, 'The Effect of Sulfide Inclusions on the Susceptibility of Steels to Pitting, Stress Corrosion Cracking and Hydrogen Embrittlement', "Werkstoffe Und Korrosion", Volume 32, No. 11, November, 1981
-

A literature review on the effects of inclusions concludes that all non-metallic inclusions occurring at the metal surface have a detrimental effect on the resistance of the steel to hydrogen embrittlement. Particularly harmful are the manganese-containing sulphides. They release H₂S as they dissolve and this compound promotes the entry of hydrogen into the metal. Internal non-metallic inclusions act as nucleation sites for hydrogen-induced cracks in high strength steels. In medium and high strength steels, the inclusions impair the metal plasticity. In high strength steels, the inclusions, with low thermal expansion coefficients compared to the steel, facilitate cracking due to increased stresses around the inclusions. Sulphides, which exhibit a higher thermal expansion coefficient, may, in some cases, affect favorably the resistance of steel to HIC by trapping hydrogen in microvoids, present around the inclusions.

- 136 K. Sieradzki of Iowa State University, 'On the Embrittlement of Steels by Hydrogen Sulfide', "Scripta Metallurgica", Volume 15, No. 2, February, 1981
-

Highly theoretical, this work describes the crack morphology in high strength steels. Although interesting, it is of no practical significance to this study.

- 137 F. Terasaki, A. Ikeda, M. Takeyama, and S. Okamoto, 'The Hydrogen Induced Cracking Susceptibilities of Various Kinds of Commercial Rolled Steels Under Wet Hydrogen Sulfide Environment', "The Sumitomo Search", No. 19, May, 1978
-

Many commercial alloys with tensile strengths of 40-80 Kg/mm² in various heat treat conditions were tested in BP type solutions. Semi-killed versus fully-killed steels were also tested. It was determined that HIC cracking was strongly dependent upon the segregation of Mn and P in the ingot. Cracking occurred in pearlite bands or in areas of untempered upper bainite or martensite. Quench-and-tempered structures produced more resistance to HIC. The possibility of HIC cracking in piping material appears to be small due to the use of smaller ingots. Lowering sulphur contents and eliminating structures prone to cracking can reduce, but not eliminate, susceptibility to cracking. Semi-killed steels appear to be more resistant than killed ones as there is less segregation. Thermal history following rolling may give an indication as to cracking tendencies. Those steels finished at lower temperatures are more apt to crack than those of high temperatures. Controlled rolling can produce structures prone to cracking. There are indications that the authors presented orally many items pertaining to cracking that were not included in this article.

- 138 Friedrich Karl Naumann, 'Hydrogen Sulfide Corrosion, Examination of a Blistered and Cracked Natural Gas Line', "Praktische Metallographie", Volume X, No. 8, August, 1973
-

A welded natural gas line of 400 mm O.D. and 9 mm wall thickness made of plain carbon steel (-0.22%C) burst after 4 months service; the line was 12 km long operating at 60 atm. The pipe had black internal film and large flat blisters. U.T. showed other delaminations where no blisters showed. Only butt welds and

their adjacent areas were crack free. Gas in blisters was found to be:

- 89.4% H₂
- 2.4% CO₂
- 7.0% N₂
- 1.7% O₂

It is postulated that the O₂-N₂ entered as air during testing and actual composition of gas was 97.4% H₂. The cracks were step-wise in nature and generally started from blisters at the centreline of the pipe. The number of defects decreased as examination moved away from the gas entry point. The pipe contained elongated inclusions; cracks propagated from these inclusions.

A section of pipe was hydrostatically tested. Pressure could be raised to 1 1/2 times operating pressure without trouble. Rupture occurred in a highly blistered region soon after the pipe passed the yield point, about 170 atm.

139 T.G. Gooch, 'Stress Corrosion Cracking of Ferritic Steel Weld Metal - The Effect of Nickel - Part 1 and 2', "Metal Construction", Volume 14, 1 and 2 January/February, 1982

Studies were made of the effect of Ni on the stress corrosion behaviour of weld metals in H₂S environments (NACE test). Nickel was found to have no major effect on stress corrosion cracking resistance or on hydrogen pick-up rate. Rather, parent metal degradation was more prevalent. However, the scatter in the results presented is such that one could equally claim that, under certain conditions, nickel had a significant effect. In addition, variations in results of extended time tests require further explanation before one could accept the conclusions. Examining the NACE test results suggests that Ni does have a detrimental effect upon the alloy resistance to sulphide solutions; however, failures took place away from the weld.

One must be cautious when considering HIC; as field experience indicates, cracking generally does not occur in welds, presumably due to the structure. Consequently, the effects of the nickel-rich welding deposit may be counter-balanced by the structure. More extensive testing with strict control of parameters is required.

140 D.D. McAusland and J.A. Webb of B.P. International, 'Development of Materials and Fabrication Requirements of Oilfield Production Valves in Sour (H₂S/Chloride) Service', "The Chemical Engineer", May, 1981

A very general paper that discusses NACE MR-01-75 and its associated problems more than the apparent subject. There are some good hints as to what B.P. found through a survey of valves in the Middle East.

Austenitic stainless steels, in the solution annealed condition, are resistant to SSC. A hardness level of Rc 22 is not consistent with what is expected in this condition; the level should be considerably lower.

The use of free-machining steels results in steels more prone to cracking due to the sulphur content and to the number of inclusions.

Failures of valves tended to be confined to the highly stressed parts.

B.P. assumes that any component can be sour and designs accordingly, i.e. - there is no safe level of H₂S. All steels must not exceed BHN 240 in hardness.

Aluminum alloys and cast iron are not used.

B.P. works with each manufacturer to develop a unique valve specification, recognizing that skills of various companies differ.

141 D.P. Dautovich, M.G. Hay, P. Mayer, B. Mulherjee and H.J. Westwood, 'Hydrogen in Metals - Hydrogen Related Problems in an Electric Utility', "CIM Annual Volume", 1978

Vessels containing moist hydrogen sulphide gas are most vulnerable to step-wise cracks and blisters. This form of attack has occurred in the absorber tower trim sections and in the rundown tanks at the Bruce Heavy Water Plant. In many cases the step-wise cracks reach the surface and develop a corresponding trench. Laboratory and field testing revealed that the cleanliness of the steel and the rate of hydrogen entry strongly influenced whether or not hydrogen damage occurred. Blisters were found to form only if pre-existing defects of a certain size were present or if hydrogen entry exceeded a critical rate. To control hydrogen damage, one would employ a very clean steel, shape control the inclusions to make them small and globular, and produce a protective scale barrier on the steel surface. Observations using a hydrogen probe indicated that hydrogen permeation was much lower in piping containing water saturated with H₂S than in moist gas situations, probably due to the formation of scales. Consequently, preconditioning to produce this scale should reduce permeation. However, the presence of as little as 2 volume percent of oxygen greatly increases the permeation rate, even with relatively impermeable scales.

142 M.G. Hay and D.P. Dautovich, 'Control of Hydrogen Induced Cracking in Low Strength Carbon Steel Exposed to Hydrogen Sulphide Environments' - First International Conference on Current Solutions to Hydrogen Problems in Steels - ASM, Washington, November, 1982

The paper outlines tests and field experience with various steels, by Ontario Hydro Research and the Bruce Heavy Water Plant. Mackinawite produced by water saturated with H₂S is more protective than that produced with gas. High hydrogen fluxes were experienced in moist H₂S gas at 30°C. These high fluxes were accompanied by negligible corrosion. In contrast, low hydrogen fluxes were obtained in aqueous hydrogen sulphide even if the corrosion rates, and hence hydrogen generation rates, were very high. Steels with hydrogen damage susceptibility of CTR greater than 9% and CLR greater than 29% have suffered rapid, severe damage in service where hydrogen fluxes reach a value of Co equals 6 μ g/g but not at lower fluxes, i.e. Co equals 3.5 μ g/g.

Steel heats were found to vary in their hydrogen damage resistance.

In addition the following were noted:

(1) Normalizing or quenching and tempering improved the resistance to HIC.

(2) Reducing the number of working (rolling) operations improved the resistance to HIC.

(3) Shape control of sulphides by rare earth additions was ineffective.

(4) Cu additions were not effective in reducing HIC resistance at low pH.

The Bruce Heavy Water Plant employs a maximum CLR of 10% and CTR of 1.5% in the modified Cotton Test to ensure adequate performance of steels in the aggressive environments at the front end of the plant.

143 M.G. Hay, 'Hydrogen Induced Cracking in Steels for Heavy Water Producing Plants' - NACE Eastern Canada Conference, Ottawa, October 3, 1979

This paper outlines the effect of hydrogen induced cracking. Corrosion in moist gas produces atomic hydrogen which penetrates steel, collecting at inclusions to form blisters and step-wise cracks. Lowering the sulphur content of the steel, forming stable sulphide scales, and raising pH or temperature all help to reduce susceptibility to HIC.

144 John A. Peterson, Donald W. Johnson and G.S. Drigel of Armco Research and Technology, 'Effect of Cooling Rate After Tempering on Sulfide Stress Cracking (SSC) of Seamless Tubular Products' - Paper presented at the 23rd Mechanical Working and Steel Processing Conference, Pittsburgh, Pa. October 28-29, 1981

Two seamless tube materials - one, a C-Mn steel with some Cr and Mo and the second, a C-Mn steel with some Mo and V, were quenched and tempered to three strength levels. Double cantilever beam specimens were used with the standard NACE test solution (aqueous 0.5% acetic acid, 5% NaCl, saturated with H₂S at 25°C) to determine threshold stress intensity values for water quench after temper and for slow cooling after temper. It is generally felt that segregation to grain boundaries of such elements as phosphorus can reduce SSC resistance of steels, particularly if tempering occurs in the embrittling range. Water quench following tempering was found to give the best results. In addition, higher tempering temperatures, beyond the embrittling zone, produced higher stress intensity values for both quenched and slow-cooled specimens. Cracking occurred along prior austenite grain boundaries. Experiments on full size pipe were not in complete agreement with laboratory samples although the same trend is observed.

This is a good paper outlining characteristics of SSC as affected by heat treatment.

145 M.B. Lawson, L.D. Martin and G.D. Arnold Haliburton Services, 'Chemical Cleaning of FeS Scales' - Paper presented at NACE Corrosion 1980, Chicago, March 3-7, 1980

This paper, only marginally related to this report, outlines various methods that can be used to remove iron sulphide scales. Acids are normally employed but alkaline solvent is also effective. All systems require some method of dealing with the H₂S gases generated.

146 'Sulfide Corrosion Cracking of Line Pipe Steel in Sour Gas Service', Nippon Kokan Technical Bulletin, October, 1981

This summary paper describes two pipe samples subjected to rigorous tests for resistance to SSC and HIC in the NACE solution and in the BP type solution.

NACE solution: 0.5% acetic acid plus 5% NaCl saturated with H₂S, pH equals 3.5

BP solution: synthetic sea water saturated with H₂S-pH equals 5.1 to 5.3

The two samples were low carbon CSA Z245 Grade 386 Category III 406.4 mm (16") O.D. x 9.53 mm (0.375") wall. They had a sulphur content of 0.001% and were calcium treated for shape control. Hardness was controlled to less than 240 BHN. No cracks or blisters were detected in any test, either in the parent material, the weld material, or the HAZ.

147 T. Taira and Y. Kobayashi of Nippon Kokan, 'Development of Line Pipe for Sour Gas Service' - Proceedings Manuscript for "150th Anniversary of the Discovery of Vanadium", The Metal Society at London, October 21-23, 1981

Full size SSC tests were carried out on six pipeline steels for the sour gas industry. The tests were carried out at 80% of the specific minimum yield, using the NACE solution. The pipes were either ordinary low sulphur or super-low sulphur, calcium treated by powder injection. Four types of cracks - straight cracks, step-wise cracks, sulphide stress cracks, and blisters - occurred in the base material. Formation of the straight cracks was completed within two weeks but the step-wise cracking continued until the end of the tests.

SSC was observed to start from a corrosion pit and to propagate perpendicular to the hoop stress. The crack, most probably, would branch and then stop propagating. SSC was also found to initiate at the centre of blisters. HIC was found to propagate along the segregation bands of the material in pearlite-, and bainite-, rich areas.

Few cracks were found in super low sulphur and calcium-treated steels. Cu-Ni additions were effective in preventing HIC with pH above 5.

Mn and P were found to increase the hardness of the material and, hence, the SSC susceptibility, particularly in the segregation bands. With quenched and tempered steels the hardness of materials with less than 1.55% Mn was reduced by the heat treatment so that SSC susceptibility was decreased. In as-rolled steels, Mn contents over 1.0% resulted in rapid hardening and greater SSC susceptibility.

Full-size tests were found not to correlate well with laboratory tests. The saturated hydrogen content of the standard HIC specimen is far greater than would be found in the actual pipe. Coating the samples resulted in a hydrogen concentration too low. One-sided testing was most representative of field conditions.

Almost no cracking was observed in the super low sulphur, calcium-treated material. For this material the standard HIC test in low pH solutions is a good indication of the crack behaviour in wet, sour gas environments.

This is an extremely good reference paper.

148 M. Kowaka and S. Nagata, 'Effects of Strength and Composition on Sulfide Corrosion Cracking of Low Alloy Steels', "Metallic Materials", 12th Japanese Congress on Materials Research, March, 1969

Studies on 16 different steel melts were undertaken to determine the effects of C, Mn, Cu, Ni, Cr, Mo, V, B and Ti upon the sulphide stress corrosion cracking resistance of steels. The steels were tested in various quenched and tempered conditions to produce martensitic and tempered martensitic structures. The test solution was H₂S saturated, 0.5% acetic acid (NACE solution). Blisters and HIC were ignored in these experiments. Steels were classified as to strength, using hardness as a criterion. It was determined that:

- (a) below Rc 19, steels with no nickel content were resistant to SSC,
- (b) between Rc 19-29, the chemical composition strongly affected the susceptibility to cracking. Ni increased the susceptibility to cracking followed by Mn, Ti, Cu and V, Mo, Cr and B had no effect on cracking susceptibility. C had no effect by itself but C, coexisting with Mn and V, did affect the cracking susceptibility, and
- (c) over Rc 29, the steels were sensitive to sulphide stress corrosion cracking regardless of chemical composition.

It should be pointed out that the steels studied always contained several alloying elements so that the effects on SSC could have been due to a combination. To be precise, other heats eliminating most of the alloys should have been employed. In addition, the authors used arithmetic means to predict failures in samples that had not cracked - without considering such factors as times.

149 S.A. Golovanenko, V.N. Zikeev, E.B. Serebryanaya and L.V. Popova, 'Effect of Alloying Elements and Structure on the Resistance of Structural Steels to Hydrogen Embrittlement', "Metal Science and Heat Treatment", Volume 20, pp 3-14, 1978

A literature survey was made on the effects of various parameters on the SSC and HIC resistance of low alloy steels.

- (1) Increasing temperature decreases the susceptibility to sulphide environments.
- (2) Rate of loading is cause for concern. HIC susceptibility is not revealed by impact tests but rather by slow loading.
- (3) Decreasing pH increases corrosion and, hence, hydrogen available for diffusion.

(4) Carbon effects on SSC are normally related to the microstructure produced. Even high carbon levels will be resistant if properly tempered structures are produced.

(5) The effects of silicon are questionable as some authorities indicate detrimental, and others, favorable results.

(6) Manganese has a negative effect on both SSC and HIC due to the formation of hard structures and to the formation of sulphide stringers.

(7) Phosphorus has a detrimental effect due to segregation and hardness.

(8) Sulphur has a detrimental effect on HIC due to the formation of inclusions. Shape control with Rare Earth Metals is advocated. This is not considered as beneficial as it was in 1978.

(9) Nickel content is controversial with some authors claiming no problems and others, severe degradation.

(10) Cu impairs weldability but is favoured by Japanese manufacturers.

(11) Al is said to have a beneficial effect. This survey was published before it was generally accepted that Al₂O₃ particles are prime sites for blistering.

(12) Raising Mo content increases the corrosion resistance and lowers the hydrogen available for diffusion.

(13) Titanium is thought to produce intergranular problems with respect to SSC.

(14) V and Nb increase the resistance to SSC.

(15) Chromium increases the resistance to SSC in quenched and tempered steels.

(16) A quench-and-tempered structure should be used to prevent Mn and P segregation.

Although published in 1978, the article tended to rely on information published much earlier. Many of the beneficial aspects reported have been discounted in later work. This is confirmed by the references; most are works of the 1950's and 1960's with only a few from the 1974 to 1976 era. Nothing later than 1976 is listed, yet extensive pertinent work was done in 1977 and 1978. Contrast this with a Japanese paper printed about the same time which has seven references from 1977 and one from 1978, as well as all the literature cited by the above paper.

150 E. Snape, 'Roles of Composition and Microstructure in Sulfide Cracking of Steel' - Presented at the 24th Annual Conference, NACE, March 18-22, 1968, Cleveland, Ohio (Classic Paper)

The sulphide cracking resistance of a number of steels containing various alloying elements and in varying heat treat conditions, was examined. It was determined that susceptibility to sulphide cracking was primarily dependent on microstructure. Steels with uniform, spheroidized carbides in a ferrite matrix

had the greatest resistance at any given strength level. The presence of untempered martensite in the matrix drastically reduced the cracking resistance. Lamellar carbides, resulting from either normalizing and tempering or isothermal transformation, gave rise to cracking resistance intermediate between steels fully quenched and tempered, and steels containing untempered martensite.

Alloying elements such as nickel were important only in the effect they had on structure. As long as the structures were properly tempered, cracking resistance was high. However, nickel tended to raise the tempering temperature beyond that normally employed to produce satisfactory structures. Consequently, Ni has the reputation of causing cracking.

151 Charles M. Hudgins, Jr., 'Practical Aspects of Hydrogen Damage at Atmospheric Temperature', "Bulletin 145", Welding Research Council, October, 1979

This paper is largely a literature survey plus some examples of problems from the author's experience. He reports blistering occurring in refinery piping and pressure vessels. Preventative measures include heat treatment, material selection, pH control and inhibition. Clean steels with strength levels below 620.5 MPa (90,000 psi) or Rc 22 equivalent should be employed. Martensitic structures and alloys must be avoided unless they can be fully tempered. Cold working can induce stresses high enough to cause cracking. Quality control and heat treatment must be employed to prevent failures.

Blisters can be vented and left, or welded up.

Non-metallic and metallic coatings can be successfully used to prevent corrosion and hydrogen penetration but they must be used with caution.

Such experience, obtained in service, is always important.

152 R.N. Tuttle, 'Selection of Materials Designed for Use in a Sour Gas Environment' "Materials Protection", Volume 9, No. 4, April, 1970

Early field experience in Western Canada suggested certain limitations on materials to be used in sour service. Hardness limits of Rc 22 and the limiting of Ni to less than 1% were determined as necessary to prevent cracking in laboratory experiments. These limits were employed to control the microstructure. Cold worked materials were found to be susceptible to failure. Weld normalization is employed on ERW pipe to prevent failure.

Materials to be Used Include:

- austenitic stainless steels - fully annealed with a hardness maximum of Rc 22
- Inconel and Inconel X-750 with maximum hardness of Rc 35.
- Hot-rolled or solution-annealed and age-hardened Monel K-500 with maximum hardness of Rc 32. (K-Monel has failed in valve stems.)
- Hastelloy B, Stellites and Colmonoys, cemented carbides.

Alloys not to be Used Include:

- low-and medium-strength steels with more than 1% Ni
- free machining steels
- cold-finished products
- precipitation hardened alloys
- ASTM A193 B7 bolts (companies still try to use these)

153 R.S. Treseder, 'Oil Industry Experience with Hydrogen Embrittlement and Stress Corrosion Cracking' - Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys - Proceeding of Conference June 12-16, 1973 - NACE Reference Book 5

An extensive review of literature outlines the various conditions that have led to problems. Essentially, cracking susceptibility increases with H₂S concentration, with decreasing pH, and with decreasing temperature. Microstructure plays an important role and hardnesses are limited to Rc 22 maximum. Heat treatment must be varied to produce desirable structures of finely dispersed carbides. Normalized and tempered or quenched and tempered structures are the best. Cold working can create problems.

A table outlining all the failures in the sour gas industry 1951 to 1972 is included.

Weld cracking was found to be a problem in the refineries using automatic equipment with certain high manganese fluxes. This resulted in weld cracking below Rc 22. Maximum hardness was recommended as BHN 200 or Rc 93. Control of welding procedures and methods is deemed critical for the safe operation of welds in H₂S environments.

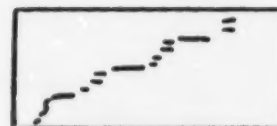
154 A. Ikeda, M. Kawaka, 'Stress Corrosion Cracking of Low and High Strength Steels in Wet Hydrogen Sulfide Environment', "Chemical and Engineering Review", Volume 10, No. 5-6, No. 117, May/June, 1978



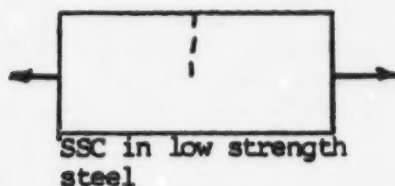
blistering



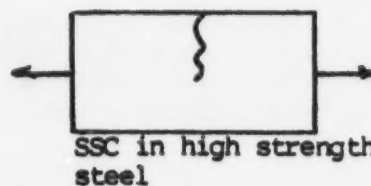
blistering, HIC & SSC



HIC



SSC in low strength steel



SSC in high strength steel

An extremely valuable paper summarizing much of the work that has been done on HIC and SSC. Cracking and/or blistering tends to occur in the segregation zones and in areas of untempered martensite and upper bainite. Shape control of carbides using Rare Earth Metals reduced HIC. In addition, reduction in sulphur content can reduce HIC. Steels containing up to 0.20% Cu show less susceptibility to HIC at pH above 5.0. Test solutions with a pH below 5 are too aggressive and do not reflect conditions in refineries (pH lower than 5 is necessary for heavy water plants). Elongated Manganese sulphides and Al₂O₃ particles act as initiation sites for HIC.

Cracking can occur if the hydrogen concentration in the steel exceeds a minimum value.

155 E. Snape, 'Sulfide Stress Corrosion of Some Medium and Low Alloy Steels' -
Paper presented to NACE South Central Regional Conference, Shreveport,
Louisiana, October 17-20, 1966 (Classic Paper)

A comprehensive study was performed of the effects of hydrogen sulphide environments on low and medium alloy steels in the NACE solution. The cracking mechanism in steels can best be described as one of hydrogen embrittlement with such factors as strength level of steel, stress level on the steel and concentration of hydrogen in the steel exerting a great influence. Delayed failure occurs when hydrogen produced by corrosion embrittles the steel to the point that fracture strain reaches the strain under load. Resistance to cracking decreases with increases in strength. Changes in alloying elements, with the exception of carbon, have no influence on cracking susceptibility. (This, of course, has been shown to be incorrect by many other authors.) Cracking susceptibility increases with carbon content. Quenched and tempered steels are the most resistant to cracking. Austenite-containing steels can absorb more hydrogen without cracking than can body-centered cubic structures.

This study overlooks the beneficial aspects of some alloying elements in combination with others. A conclusion on alloying elements was premature as much more study was needed. Snape's later paper addresses this aspect.

156 W.D. Storey of Hudson's Bay Oil and Gas Company Limited, 'Hydrogen Sulphide Corrosion of Metals', "Oilweek, May 20, 1963

Although this is called a Classic Paper, it is very simplistic.

This a very basic paper on the effects of H₂S in the oil and gas industry places some emphasis on case histories, although the cases are not described in detail. H₂S attack is described in terms of general corrosion, pitting corrosion, stress corrosion cracking and hydrogen stress cracking. In general, it has been found that high strength tubulars fail by cracking due to the presence of martensite. Inhibitor injection can control the corrosion and hence, the amount of hydrogen for entry into the steel. Oil storage tanks have been found to suffer severe blistering on the bottom and on the underside of the roof where water accumulates. Dehydrators for drying H₂S gas have also suffered severe blistering. Gathering line corrosion has not been severe due to inhibitor use. Iron sulphide scales, if they remain intact, offer corrosion protection and less

hydrogen for entry. Inspection involving ultrasonics, coupons and test spools, and hydrogen probes is used on a continuing basis to detect corrosion problems.

157 R.N. Duncan, 'Materials Performance in Khuff Gas Service', "Materials Performance", July, 1980

Severe erosion/corrosion problems were experienced in valves, piping and heat exchangers at the Bahrain Khuff gas field. Erosion in wellhead manifold and control valves was attributed to velocities in excess of 6 m/sec. Corrosion inhibitors were used effectively downhole and to control piping attack. However, severe tube end erosion resulted in leaking heat exchangers, probably due to two-phase flow. Cracking of valve components was encountered when hardness limitations were exceeded, resulting in broken seats, plugs and balls. Corrosion monitoring was considered difficult due to the erosion/corrosion. Ultrasonics and radiography appeared to be most useful. Hydrogen probe results were unsatisfactory, seemingly due to improper maintenance and a lack of understanding.

The problems outlined in this paper could have been avoided through proper quality control on design and installation. Deviation from standards should not have been permitted.

158 L.A. Jean, 'Problems and Techniques in Producing Gas Wells in Southwest France' - Erdöl - Erdgas "Zeitschrift", Volume 89, March, 1973

Corrosion in tubes occurs at low points in the form of pits. Corrosion in gathering lines was attributed to low velocities in the inhibited system.

This article reports only successes and minor problems. Other articles on problems in this field, are still unavailable.

159 Lutz Speel, 'Corrosion Control in German Gas Wells', "Materials Performance" August, 1976

Sulphide stress corrosion cracking is experienced if the NACE guidelines of RC 22 are exceeded. Austenitic stainless steels and high nickel alloys are used for special installations. Inspection involves a weekly chemical analysis, as well as coupon tests and corrosometer probes, but these are not suitable in two-phase flow conditions. Tube calipers can cause corrosion problems.

160 L.W. Vollmer, 'The Behaviour of Steels in Hydrogen Sulfide Environments', "Corrosion", July, 1958

Failure of 9% Ni downhole tubing from Pincher Creek was investigated in the laboratory, revealing sulphide stress corrosion cracking as the culprit. Materials were heat treated to hardness in the Rc 24-26 region. Plastic deformation greatly increased the susceptibility to cracking but it is not necessary if the protective scales are broken and the hardness is in the Rc 24-26 region. Metallurgical structure was considered to have an influence on the resistance to cracking. Cracking may be avoided by changing the steel composition.

161 Dave Palmer, 'Three Views of Gas-Plant Corrosion', "Canadian Chemical Processing", February 1977 - The Canadian Region Western Conference of NACE, held in Calgary, February 18-20, 1976

Hydrogen blistering was outlined as requiring the following:

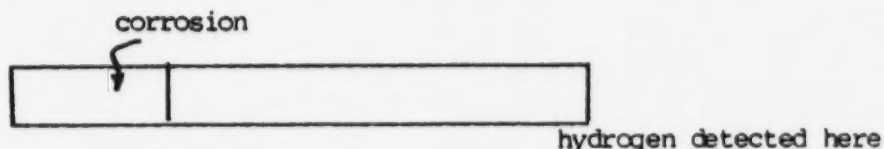
- (a) a source of atomic hydrogen,
- (b) process streams high in moisture,
- (c) a poisoning agent such as H₂S to prevent recombination of hydrogen,
- (d) imperfections in the steel, and
- (e) a low pH to retard scale formation.

Hydrogen blisters occur parallel to the rolling direction while fissure cracks occur perpendicular to the plate surface. Fissures also occur in welds and castings. Inhibitors can be successfully used to prevent corrosion.

162 E.C. French and L.R. Hurst, 'Hydrogen Monitoring by the Hydrogen Patch Probe' - Paper 47 presented at NACE Corrosion 1980, Chicago, March 3-7, 1980

A description is given of hydrogen patch probe operation wherein the hydrogen passing through a tube wall is collected in an electrolyte and the current to oxidize the hydrogen is a direct measurement of the amount of hydrogen present. It was determined that corrosion rate, poisons, temperature, and metal thickness all affected the hydrogen diffusion. Increases in corrosion rate and temperature resulted in increased hydrogen diffusion. The thicker the metal, the slower the diffusion rate. The presence of poisons, such as sulphur compounds preventing the recombination of hydrogen, also increased the diffusion rate.

Hydrogen also was found to diffuse from remote areas.



163 G.J. Bieffer, 'The Environmental Cracking of Line-Pipe Steels - A Short Review', "Mines Branch Information Circular IC295", November, 1972

A literature review was made of selected articles relating to cracking of pipelines. Three failure categories are listed: Sulphide Cracking, Hydrogen Embrittlement Cracking and Stress Corrosion Cracking depending on the assumed source of failure. Sulphide cracking is the predominant mechanism outlined and hydrogen embrittlement cracking may be considered as a similar phenomenon produced by cathodic charging of the steel.

Sulphide cracking failures were found to originate primarily from the inside of the pipe in steels with hardnesses exceeding Rc 22 (772 MPa or 112,000 psi tensile strength). They occurred in environments containing as little as 1 ppm of sulphide. Fracture usually occurred in regions of high hardness such as HAZs of welds or segregation structures where untempered martensite could exist.

Structure appears to be most important in determining response to cracking as some authors recorded failures considerably below Rc 22 and no failures in harder material, depending on the structure. Decreasing pH increased susceptibility to cracking although one author claims no effect between 2 and 5. Cold working increases the tendency to crack. Chemical composition is critical, particularly with respect to Ni, as local hard spots can be induced due to a lowering of the critical temperature so that tempering produces austenite that can transform to martensite. Welding generally reduces the resistance to cracking. Room temperature is said to be the most damaging temperature with decreases in cracking occurring as the temperature is raised or lowered.

Sulphide cracking increases in severity with increasing H₂S, decreasing pH and increasing applied tensile stress.

The author, in a recent discussion, considered this paper "naive" in relation to his more recent publications and one tends to agree. However, in fairness it should be noted that only selected references were quoted and consequently, a narrow view of the problem was presented.

164 G.J. Bieffer and M. Fichera of Energy Mines and Resources, 'Examination of Steel from Two Failures in the Grizzly Sour-Gas Pipeline', "Canmet Report" MRP/PMRL 82-3 (GF), March, 1982

Two failures occurred in Westcoast Transmission Company's Grizzly Pipeline in British Columbia in July 1981. The pipe was Grade 359 spiral-weld 508 x 9.5 mm (20" x 0.375") pipe. Operating life to failure was 17 months with 27.5% H₂S natural gas at a pressure of 6-7 MPa (900-1000 psi). Fractures occurred in the weld and the HAZ.

All cracks were associated with spiral welds and fell into three categories.

- (a) cracks in weld metal transverse to the weld direction - WT.
- (b) cracks in weld metal parallel to weld direction - WL.
- (c) cracks parallel to the weld in the HAZ - HL.

Cracks in the heat affected zone were found to have some step-wise cracking tendencies. These were most evident in the middle third of the pipe wall.

No hardening of the HAZ was found except for one spot.

Failure was due to SSC on the weld face and in the heat affected zone in material that was generally less than Rc 22 in hardness. It is felt that stresses and environment were extremely severe, causing failure of a normally resistant steel. SSC propagated through sufficient wall thickness to cause rupture of the remaining metal through mechanical overload.

Some testing of welds might be in order as submerged arc welding can produce welds prone to SSC under certain conditions. Treseder has reported that Rc 93 is the limiting hardness to prevent failure in some automatic submerged-arc welds.

165 G.J. Biefer, M. Fichera and J. Selwyn, 'Stepwise Cracking Behaviour of Some Canadian Line Pipes', "Canadian Metallurgical Quarterly", Volume 22, No. 2, 1983

Samples of five gas transmission pipes were subjected to step-wise cracking (HIC) tests in the BP Test Solution (relatively mild conditions). A semi-killed and four fully-killed steels were tested.

Two steels, the semi-killed and another, both with the largest, elongated, sulphides, showed cracking in all locations but most notably at the welds. The other three steels showed little or no cracking in weld HAZ's but did exhibit cracking elsewhere. Segregation can probably account for the cracking susceptibility at 90° and 180° away from the weld. Semi-killed steel is probably more resistant to SWC than some of the fully-killed steels as per Moore and Warga (Ref. 7). In addition, the Cu content of the semi-killed steel was high enough to retard cracking through film formation which prevented hydrogen entry.

Step-wise cracks were few in number, probably due to the mild conditions of the test. pH is a major variable in influencing step-wise cracking; the lower the pH the greater the tendency to crack.

The samples with the most elongated MnS inclusions showed the greatest amount of SWC.

166 Y. Nakai, H. Kurahasi and N. Totsuka, 'Hydrostatic Burst Test of Pipe with HIC' - Paper 133 - Corrosion 1982 NACE, Houston, March 22-26, 1982

The bursting pressures of pipeline steels that had suffered varying degrees of hydrogen-induced cracking were investigated by performing hydrostatic tests on sections of line pipe. It was determined that HIC reduces pipe properties and in the case of severe damage can result in rupture at pressures below those necessary to produce yielding. Hydrogen embrittlement was found to occur at the tip of the HIC with the new crack propagating towards the inner surface of the pipe, perpendicular to the hoop stress direction.

In addition, it was proposed that corrosion tests should be performed on one side of pipe material only, to approximate service conditions. Under these conditions pipe with an HIC of less than 30% of the ratio of crack area by UST in the BP Test, will not experience HIC in a one-sided test.

167 E.L. Hildebrand of Humble Oil and Refining Company, Baytown, Texas, 'Aqueous Phase H₂S Cracking of Hard Carbon Steel Weldments - A Case History', Proceedings Division of Refining, Amercian Petroleum Institute, Volume 50, 1970, pg. 593-613

A light ends fractionation unit designed to process hydrocarbon feed containing up to 2% by volume of hydrogen sulphide suffered hydrogen embrittlement and cracking of hard weld deposits in four major carbon steel pressure vessels after three weeks service. The longest crack was 280 mm (11").

A new facility replacing one that had operated 30 years without problems experienced leaks on the 21st day after start-up. Dripping liquid and vapour was found to be coming from three cracks. The main crack was 280 mm (11") long and extended approximately 127mm (5") on either side of a longitudinal submerged arc weld. The other two cracks were 25 mm (1") long and were in the weld deposit. Internal inspection revealed 300 cracks - all transverse and all contained in submerged arc weld deposits. Closing head welds made by manual metallic arc contained no cracks.

Two other vessels by the same manufacturer had cracked welds.

Chemical analysis revealed Mn and Si twice the allowable to ASME Code. Hardness readings were 235-255 Brinell. Piping and other vessels welded with MIG and submerged arc also showed higher hardness than the allowable but had had a manual arc stringer or back weld preventing the cracking.

Welding procedures for the submerged arc process permitted the use of filler metal and flux known to produce high manganese and silicon which also contribute to high hardness.

Microhardness tests showed areas with hardness over 300 BHN.

These areas of high hardness, high manganese and silicon content did not respond to conventional heat treating procedures.

A hardness survey on other vessels indicated that many submerged arc welds and some MIG welds exceeded the hardness limit of BHN 235 or Rc 22. These welds usually contained high Mn and Si contents.

This article gives a good description of the problems encountered.

168 J.G. Morris and B.J. Roopchand, 'Metallurgical Structures to Resist Hydrogen Embrittlement in Ferrous Alloys', "Proceedings of Conference Environmental Degradation of Engineering Materials", Blacksburg, Virginia, October 10-12, 1977

Multiphased ferrous alloys are embrittled by hydrogen with the embrittling tendency being less for a pearlitic structure than for a bainitic or martensitic structure. Even one-phase systems can be embrittled if the carbide is not spherical in shape.

169 R. Carber and I.M. Bernstein, 'Effect of Microstructure and Manganese Content on the Hydrogen Embrittlement Susceptibility of Medium Strength Carbon Steel', "Proceedings of Conference Environmental Degradation of Engineering Materials", Blacksburg, Virginia, October 10-12, 1977

The effect of varying manganese contents from 0.1 to 2.6 wt % on hydrogen susceptibility of fully pearlitic or fully spheroidal eutectoid carbon steel was examined for yield strengths up to 689.5 MPa (100 Ksi). At strengths near 690 MPa (100 Ksi), pearlitic steels were more severely embrittled than spheroidal steels - independent of manganese content. Mn has a significant effect on cracking under stress corrosion conditions.

- 170 L.N. Pussegoda and W.R. Tyson of Canmet, 'Relationship Between Micro-structure and Hydrogen Susceptibility of Some Low Carbon Steels' - Hydrogen Effects in Metals Conference - Proceedings 3rd International Conference on Effect of Hydrogen on Behaviour of Materials - The Metallurgical Society of AIME, Moran, Wyoming, August 26-31, 1980
-

Slow tensile testing was carried out on alloys and concluded:

(1) A low-carbon, martensite-bainite structure has greater susceptibility to hydrogen embrittlement than does fine-grained acicular ferrite of similar hardness.

(2) A direct-quenched, fine-grained steel has better resistance to hydrogen embrittlement than does a quenched and tempered material even though the strength is greater.

(3) Electroslog-welded material has the lowest hardness but reveals the greatest susceptibility to hydrogen embrittlement with increasing temperature.

- 171 M. Iino, N. Nomura H. Takezawa and T. Takeda of Nippon Kokan, 'Engineering Solutions to the H₂S Problems in Linepipes', "Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels", Washington D.C., November 1-5, 1982
-

A number of laboratory and commercially prepared steels were tested by immersion and constant strain rate tests in synthetic sea water saturated with H₂S with pH varied by acetic or hydrochloric acid. pH for strain rate tests was 3.0 - 3.8.

At pH 5.3 microalloying with group VIII elements (Ni, etc.) reduces the hydrogen entry into the steel. Similarly, alloying with elements such as Au, Cu and Cr has the same effect. At pH of 4.0 Cu and Cr lose their effect but the VIII elements appear to be still effective. Cu with Mo is seen to greatly increase corrosion rate and hydrogen entry.

Shape control using calcium proved effective in reducing susceptibility to hydrogen damage.

Heat treatments that temper bainitic and martensitic structures, preferably followed by quenching, greatly reduce the susceptibility to HIC, provided the steel does not contain a banded structure.

If a banded structure is present, the quench following tempering is mandatory to produce a resistant structure.

- 172 Dale McIntyre and Carlo Sonnino, 'Hydrogen Embrittlement of PH 13-8 Mo Steel' - 2nd International Congress on Hydrogen in Metals, Paris, France June 6-11, 1977
-

(1) PH 13-8 Mo stainless steel is highly susceptible to hydrogen gas embrittlement and is not be used where hydrogen gas exposure is required.

(2) PH13-8 Mo stainless steel is susceptible to internal hydrogen embrittlement but less than other low-alloy steels of the same strength level.

(3) Fracture mode is a function of the aging temperature of this alloy.

173 T. Nishimura, H. Inagaki, and M. Tanimura, 'Hydrogen Cracking in Sour Gas Pipeline Steels' - Paper 3E9, Second International Congress on Hydrogen in Metals, Paris, France, June 6-11, 1977

Various steel samples from API 5LX-X42 to X65 grade steels were tested in H₂S saturated synthetic sea water, pH 5.2. It was determined that hydrogen cracking originated at MnS inclusions (Type II) in the absence of external stress. Lowering the sulphur content of the steel could lower the cracking susceptibility. Normalizing and quench-and-tempering, also lowered the susceptibility.

The addition of copper improved the cracking resistance by producing a tightly adherent scale. However, copper added to steel containing over 0.1% Mo markedly increased the cracking susceptibility and the general corrosion rate. Manganese above 1.80% and nickel above 0.60% greatly improved the cracking susceptibility, again by producing a surface scale.

174 G.F. Taylor, 'The Corrosion of Steel in Heavy Water Production - Operating Experience and Laboratory Development' - Proceedings of the 7th International Congress on Metallic Corrosion 4, 1536, Rio De Janiero, 1978

Experiments carried out at CRNL indicated that carbon steel could be given a protective sulphide layer by exposing it to warm hydrogen sulphide solutions (125°C) for periods up to 14 days. The film produced, generally pyrite and pyrrhotite, drastically reduced the corrosion rate of carbon steel exposed in both laboratory test loops and heavy water plant exposures. However, if the iron levels in the solutions is below saturation, the formation of the protective sulphide is retarded. In addition velocities must be such as not to remove the sulphide layers - lower than 2.1 m/sec.

175 H. Okada, E. Sato, and T. Murata, 'Internal Blistering of Linepipe Steels' - Presented at Corrosion/77, San Francisco, March 14-18, 1977

Investigation carried out on a X65 pipeline steel under BP Test conditions indicated that internal blistering always occurred at inclusion colonies of Type II Manganese sulphide stringers that had been elongated during hot rolling. The driving force for the blistering was said to be hydrogen gas pressure with the hydrogen generated by corrosion on the metal surface. The hydrogen entry is governed by pH (low pH-greater corrosion), temperature (blistering was suppressed above 60°C) and alloying elements (Cu and W greatly reduced hydrogen entry). In addition, control of the segregation of Mn, P and Si was felt to suppress blistering. Shape control by rare earth metals was also helpful although sulphur control also would be necessary.

- 176 A. Ikeda, Y. Morita, F. Terasaki and M. Takeyama of Sumitomo, 'On the Hydrogen Induced Cracking of Line Pipe Steel Under Wet Hydrogen Sulphide Environment' - Paper 4A7 Second International Congress on Hydrogen in Metals, Paris, France, June 6-11, 1977
-

Testing of pipeline steels under BP Test conditions was conducted. The concept of a critical hydrogen level (Co) below which cracking would not occur was advanced. Copper additions to the steel were said to prevent hydrogen absorption and, hence, reduce HIC susceptibility.

HIC, although occurring without the application of external stress, can be accelerated by external stress. However, SSC requires the application of external stress close to the yield point and HIC almost always occurs along with SSC in low-strength steels.

Predeformation, if it is small, can have a beneficial effect on HIC whereas a 20% or more cold reduction can result in increased crack length.

A step-wise cracking mechanism is proposed as follows:

- (a) separation between matrix and inclusions occurs in the early stage and plastic deformation assists it;
- (b) hydrogen embrittlement occurs in plastic regions; and
- (c) a crack propagates in the direction normal to tensile stresses.

This is a relatively early paper by A. Ikeda and the Co theme is more fully developed in his later publications. Nonetheless, it does identify a cracking mechanism that has been widely studied.

- 177 C. Parrini and A. DeVito, 'High-Strength Microalloyed Pipe Steels Resistant to Hydrogen-Induced Failures', Micon 78: Optimization of Processing Properties, and Service Performance Through Microstructural Control, ASTM Houston, 1979, pg 53-72
-

Extensive testing carried out on X42 to X80 pipeline steels, generally under BP Test conditions, led to the following conclusions:

- (1) The SSCC mechanism is strongly influenced by the steel's tensile properties.
- (2) Microstructures can be arranged in the following order of decreasing resistance to SSCC: upper bainite, lower bainite, tempered martensite, ferrite/pearlite and untempered martensite. However, the authors caution that resistance may vary in different environments. This would be in agreement with other authors who claim that upper bainite can be quite susceptible to SSCC.
- (3) Chromium, silicon, and aluminum were found to have a beneficial effect in preventing cracking while manganese, copper and nickel were found to be detrimental.

(4) There was no apparent difference between as-rolled, control-rolled, or normalized products provided they have the same microstructure. This is in contrast to field trials and studies done by various Japanese authors who, indicate a strong influence in the rolling operation, particularly with respect to hydrogen induced cracking.

(5) There is a strong influence of non-metallic inclusion morphology, particularly in relation to the toughness of flat-rolled products. Shape control of sulphides through use of Rare Earth Metals, calcium, zirconium, manganese and other treatments can be beneficial. However, niobium and vanadium can have detrimental effects due to their dispersion-strengthening tendencies.

(6) It was possible to protect the HAZ from SSCC by means of a galvanic couple through the proper selection of weld metal composition. Coupling could be equally dangerous, however, if hard welds are produced and they crack.

178 J.B. Harrell, 'Corrosion Monitoring in the CPI', "Chemical Engineering Processing", March, 1978

This general paper outlines various methods of testing that can be used in industry. The methods discussed are:

- (a) weight loss coupons,
- (b) pressure type hydrogen probes,
- (c) electrical resistance type thickness measurement,
- (d) linear polarization corrosion rate measurement,
- (e) hydrogen penetration rate measurement, and
- (f) potentiodynamic polarization measurements.

This is a good introduction to the methods.

179 V.N. Kudryavtsev, Kh.G. Schmitt-Thomas, W. Stengel, and R. Waterschek, 'Detection of Hydrogen Embrittlement of a Carbon Steel by Acoustic Emission' "Corrosion", Volume 37, No. 12, December, 1981

A Type CK 35 steel (0.35% C) was electrochemically charged with hydrogen. Acoustic emission analyses were correlated with the conditions of hydrogen charging and the analytically measured hydrogen content. A correlation between the acoustic emission signals and the embrittlement of the material can be found if the material is loaded up to the yield strength, unloaded, and reloaded. Material without hydrogen embrittlement shows acoustic emission in the second load phase only if the level of the first load is exceeded. Hydrogen embrittled material will show acoustic emission signals in the second load phase even below the level of the first load phase.

The work holds promise for future laboratory studies, but field trials under plant operating conditions would be necessary to outline practical aspects before one could accept the authors' conclusion on field applications.

- 180 D.L. Sponseller, R. Garber and J.A. Straatmann, 'Effect of Microstructure on Sulfide-Stress-Cracking Resistance of High-Strength Casing Steels' - Micon 82: Optimization of Processing, Properties, and Service Performance Through Microstructural Control, ASTM, Houston, 1982
-

Laboratory and commercial heats of high strength material were investigated in a bent beam and a three-point load test. The following was determined:

- (1) Totally unworked (cast) structures displayed excellent resistance to SSC (found by others for welds, also).
- (2) A fine, prior austenite grain size promotes good SSC resistance in the quenched and tempered steel product.
- (3) Martensite leads to greater SSC resistance after tempering than does bainite at yield strengths above 690 MPa (100 Ksi).
- (4) The SSC resistance is raised markedly by increasing the tempering temperature with the attendant coalescence of carbides and lowering of dislocation density, even if the tempering times are shorter at the higher temperature.
- (5) Extremes of tempering temperature - either above the AC1 or in the temper-embrittlement range - have a detrimental effect upon SSC.
- (6) The cooling rate after tempering can have a considerable effect on SSC resistance. Water quenching affords the maximum resistance.

- 181 G. Philipponneau, M. Habashi, J. Galland, and P. Azou (France), 'Effects of Copper Addition in Mild Steels Under Cathodic Polarization Potential and H₂S Environment' - Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, Washington D.C., November 1-5, 1982
-

The effects of copper additions on carbon steels were studied in the NACE solution at pH 3 and in synthetic seawater at pH 1. Both solutions had 3000 ppm of H₂S continuously bubbled through. It was determined that at pH below 2 the addition of copper has a beneficial effect on the dissolution potential, weight loss and ductility loss. Above pH 2, the delayed rupture time is decreased. In the NACE solution copper has a harmful effect upon delayed failure tests at cathode polarization potentials due to higher hydrogen solubility. The beneficial or harmful effect of copper depends upon solution composition, pH, cathodic polarization potential and external stresses.

- 182 T. Taira, Y. Kobayashi, K. Matsumoto, S. Matsumoto, T. Terunuma and K. Arikata of Nippon Kokan, 'Resistance of Pipeline Steels to Wet Sour Gas' - Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, Washington D.C., November 1-5, 1982
-

Tests were carried out on a number of steels, both control-rolled and conventionally rolled, to determine HIC and SSC resistance. Test solutions involved

BP conditions, but also H₂S saturated water and the old NACE solution at a lower pH were used for HIC testing. The standard NACE solution was used for SSC testing although the test time was decreased to 500 hours.

It was determined that passive films such as that produced by copper under high pH conditions are unreliable as a corrosion preventive because this method is too dependent upon solution composition and pH. Chloride ion and a pH over 4.8 are necessary for corrosion inhibition. Copper additions in H₂S saturated water can result in high corrosion rates and higher HIC.

Complete shape control and extensive desulphurization are necessary to eliminate HIC initiation sites. Calcium treatment appears to be the most effective.

Restricting the hardness of the segregation zones below 300 HV is also essential for complete elimination of HIC because the hard band structures containing bainite/martensite are susceptible to hydrogen embrittlement and are also a likely site of HIC. The formation of a low temperature transformation microstructure depends upon the hardenability of steel, while the hardness of the low temperature transformation microstructure principally depends upon the carbon content. Therefore, reducing the manganese content below 1% or reducing the carbon content below 0.22% improves the HIC resistance significantly.

Complete elimination of inclusions improved the SSC resistance as well as the HIC resistance. In a highly stressed specimen, fine planar-oriented cracks tend to form rather readily in pearlite. Therefore, homogenization of microstructures, which can be attained by reducing the carbon content below 0.02% or by quenching and tempering, also improves SSC resistance.

This is a good paper summarizing many aspects of the study undertaken by Nippon Kokan.

183 A. Coolen, M. Poupon, B. Lefebvre, Y. Provou (France), 'Manufacture of Welded Pipes for the Transport of H₂S Bearing Gas' - Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, Washington D.C., November 1-5, 1982

Tests carried out on steels produced in France indicate that rolling practice and chemical composition of steels are critical to HIC resistance. Manganese content should be limited to 1% to control segregation. In addition, it was indicated that calcium treatment may not be necessary to prevent HIC provided segregation is controlled. However, steels successfully resisting HIC were those with low Mn and very low sulphur, calcium/silicon treated for shape control, and controlled-rolled to produce desirable properties.

This paper seems to be a sales promotion. The chemical composition of the steels was not fully addressed by the authors and some of the resistance to HIC could have been the result of some trace elements.

- 184 R.T. Hill and M. Iino, 'Correlation Between Hydrogen-Induced Blister Cracking of Stressed and Un-stressed Specimens' - Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels Washington D.C., November 1-5, 1982
-

Both stressed and unstressed specimens should be tested because there is no correlation between critical potential for HIC in the unstressed state and that in the stressed condition. Blistering is a process of relaxing the internal gas pressure and cracking is a process of relaxing the stress field caused by externally applied stress.

This is a fairly simple paper which outlines some considerations of hydrogen damage in low and high tensile strength materials.

- 185 C.M. Pressouyre, R. Blondeau, G. Primon, L. Cadieu, 'Very Low Inclusion and Impurity Content Steels as a Solution to Resist Sour Environments' - Proceedings of the First International Conference on the Current Solutions to Hydrogen Problems in Steels, Washington D.C., Nov. 1-5, 1982
-

Steel samples were subjected to the NACE T1F 20 proposed procedure to test various steels for resistance to HIC. It was concluded that HIC-immune steels can be produced as long as the sulphur content is below 0.002% and the phosphorus content is below 0.007%. Below these concentrations the sulphide inclusions tend to get rounder, finer and more homogeneously distributed with less micro-segregation at the interface and in the neighbouring structure.

Above the critical content levels, HIC may develop as the sulphur content increases. This increase is related to the phosphorus content and to the microstructure. Oxide stringers must be avoided. Clean steels are generally manufactured with hot ladle processing.

This paper is a relatively basic one, restating work done by the Japanese much earlier.

- 186 B. Lefebvre, G. Guntz, Y. Provou, 'Behaviour of Longitudinal Welds of Pipes Exposed to the Action of H₂S' - Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, Washington D.C., November 1-5, 1982
-

Tests were carried out on welded samples using the NACE T1F20 proposed method for HIC and a 4-point bend test for SSC. It was determined that the welded zone showed no HIC. HIC initiated almost entirely in the parent metal and was associated with inclusions and hard spots. Calcium treatment for shape control greatly reduced HIC. Transformation microstructures assisted in the propagation of cracks.

Internal cracking in the parent metal was revealed by ultrasonics.

Only one sample failed by cracking, but this is not unexpected under the mild test conditions used.

This paper, again, is rather basic and extremely limited in scope. Further work should be done to test other welding techniques and Tee joints in which stress conditions might cause more problems. However, it does confirm the field experience that HIC does not occur in welds.

187 P.W. Rice, 'Evaluating Nickel Base and Stainless Alloys for Subsurface H₂S Service' "ASME Publication" 77-Pet-16

A series of tests on nickel-base alloys and some precipitation-hardening alloys was conducted, using constant strain rate procedures (C-rings). Galvanic coupling to carbon steel was also utilized. Results indicated that the high-nickel alloys showed good resistance. Martensitic precipitation hardening alloys were considered acceptable with double overaging treatments. Test results indicated cracking so acceptance is questionable. A 9% Cr - 1% Mo martensitic alloy quenched and tempered to a HRC of 19 showed good resistance.

188 O. Vosikovsky and R.J. Cooke, 'An Analysis of Crack Extension by Corrosion Fatigue in a Crude Oil Pipeline' "Int. J. Pres. Ves. and Piping", (6), 1978

Investigations were carried out on API 5LX 52 material following four failures in a pipeline during a six-month period. Three ruptures occurred in service and one during hydrostatic testing. The pipeline, 864 mm (34 in) diameter by 7.114 mm (0.281 in) wall thickness had operated approximately five years prior to the failure. Hydrogen sulphide in the crude oil was felt to be responsible for the failure.

Cracking originated in the toe of the longitudinal weld in areas of Rc 30 hardness versus the Rc 20 exhibited in other areas of the heat affected zone. Metallographic examination revealed branched cracking, preferential pitting and the development of cracks related to non-metallic inclusions. Deformation of the pipe during assembly probably produced high residual stresses.

Fatigue crack growth rate data were generated by testing samples of an API 5LX 65 linepipe in H₂S saturated crude oil. This revealed that fatigue crack growth rates increased substantially in the sour environment compared with in air.

It was determined that defects to pipe wall thickness ratios of between 0.15 and 0.20 would be required to create a fatigue failure within the five year life exhibited by the pipeline. However, if cracks or defects approaching a critical depth were present, it was concluded that a hydrostatic test could result in extension of the crack. Growth of the crack to the critical size for failure during operation, would occur in less than four months. Hence, the advisability of periodic hydrostatic testing is questionable.

Crack-like defects can grow to a critical size for rupture in operating pipelines carrying H₂S-contaminated crude oil through corrosion fatigue.

This paper confirms many others reporting pipeline failures in that cracking generally originates in hard areas such as the toe of the weld. Corrosion fatigue is often overlooked as a failure mechanism and it often results in

failure. However, the paper would be even more valuable had the authors investigated the corrosion fatigue characteristics of the failed pipeline material X52 and compared them with the X65.)

189 M. Iino, 'The Extension of Hydrogen Blister-Crack Array in Linepipe Steels' "Metallurgical Transactions", Volume 9A, November, 1978

Hydrogen induced fracture of linepipe steels is characterized by the formation of internal blisters caused by hydrogen precipitation at an inclusion-matrix interface, followed by the formation of a blister-crack array (cracking the region connecting the blisters through the actions of the internal pressure and the external stress.)

The manner of extension of the hydrogen-induced fracture is influenced by the presence of external stress as follows:

(1) In the absence of an external stress, fracture develops by step-wise linking of blisters. Considerable plastic deformation accompanies the step-wise linking.

(2) In the presence of an external stress, below the yield strength, fracture develops by linking the blisters formed in a stacked array, approximately perpendicular to the stress axis, with the blister size and spacing about 100 μ . The linking between blisters takes place with the aid of microcracks; it is characterized by the absence of the large plastic deformation observed in tests with no external stress.

(3) With an external stress near the yield strength, fracture develops by linking hydrogen embrittlement cracks generated in slip bands and the fracture surface is generally slanted at a 45 degree angle to the stress axis.

The author has used a stress analysis around a hydrogen induced crack-like cavity to explain the extension of cracks in carbon steel due to hydrogen sulphide action. The calculations generally support the views held by other studies and may be used to explain crack morphology found in service. However, laboratory prepared heats were used rather than commercial alloys. While it is often desirable to use alloys that will demonstrate specific ideas one is always open to accusations of attempting to suit the alloy to the theory. Commercial heats might have been used.

190 Y. Yoshino, 'Metallurgical Influences on the Hydrogen Uptake by Steel in H₂S Environment', "Corrosion", Volume 39, No. 11, November, 1983

The author exposed nine steels of varying composition to the 5% sodium chloride, 0.5% acetic acid, H₂S saturated solution for 96 hours. pH was initially 2.5 and rose to 3.5 by the end of the test. Hydrogen uptake was measured and was found to vary significantly with microstructure and chemical composition. It changed in very close association with the secondary precipitation hardening process - hydrogen entry was enhanced by the precipitation of M₂₃C₆ and (Fe, Cr)₇C₃ carbides but such enhancement diminished as the overaging process took place. The precipitation of fine carbide particles was said to provide sites to trap

hydrogen at the carbide interface and increase the amount of hydrogen absorbed. (Fe, Cr)₇C₃ carbide appeared to have a larger binding energy with hydrogen than MO₂C carbide because the Cr-containing steels absorbed hydrogen to a significantly greater extent. Cementite of Cr steels had only a minimal effect in hydrogen uptake in tempered martensitic structures, but it absorbed large amounts of hydrogen in upper bainite. Hydrogen uptake increased with Cr content of the steels up to 17%. However, the hydrogen uptake was practically the same for all Cr contents when the steels were in the as-quenched martensite condition.

This is an extremely interesting article but some of the alloys tested contained significant amounts of Cu and Al. Similarly, the manganese content of the Ni-2 Cr-MO alloy is significantly higher than the others tested. Consequently, some of the enhanced hydrogen uptake may be due to the presence of these alloying elements (as reported by other authors). This consideration was not addressed in the present work.

191 Alexander R. Troiano, 'The Role of Hydrogen and Other Interstitials in the Mechanical Behaviour of Metals', "Transactions of the ASM", Volume 52, 1960

In the Campbell Memorial Lecture of 1959, the author proposed that the role of hydrogen and other interstitial species in Hydrogen Environment Cracking and Hydrogen Stress Cracking, is due to the influence of the atomic bond breaking at a crack tip; hence it is related to the interatomic cohesive force. Hydrogen results in a reduction of the cohesive force of the metallic bonds and when combined with a high triaxial stress results in an elastic separation of the bonds.

An incubation period is associated with the cracking; and this period is strongly influenced by the level of hydrogen. However, the diffusion rate of hydrogen is influenced by the application of stress and when sufficient hydrogen has concentrated in a region, a crack is initiated. The implication is that crack propagation is a discontinuous process and consists of a series of crack initiations. The most severe triaxial stress state will occur just in advance of the crack. When the critical hydrogen concentration is attained, a small crack forms and grows through the hydrogen-enriched region, joining the previous crack. Further crack growth must await diffusion of hydrogen to the new region of high stress.

This theory, in combination with the hydrogen pressure theory, is generally considered to best describe hydrogen environment embrittlement and Hydrogen Stress Cracking.

192 N.J. Petch, 'The Lowering of Fracture-Stress Due to Surface Adsorption', "Phil. Mag.", Volume 1, pg 331 (1956)

Calculations are presented to suggest that hydrogen adsorbed onto the internal surfaces of cracks will reduce the surface energy and the release in strain energy will be decreased, satisfying the condition for crack propagation.

However, this theory is generally related to reversible reactions. Crack paths could be through grains or in grain boundaries, resulting in complex irreversible events. The moving crack would have to be always covered with adsorbed hydrogen and constraints might make this impossible for more than a few atom diameters from the tip. In addition, the surface energy concept is not specific to hydrogen and other species which are adsorbed more strongly than hydrogen are not equally as potent as embrittling agents.

193 C.D. Beachum, 'A New Model for Hydrogen-Assisted Cracking (Hydrogen Embrittlement)', "Metallurgical Transactions, Volume 3, February, 1972"

This paper outlines a "new model" for hydrogen assisted cracking (HAC) which seeks to explain decreasing microscopic plasticity and changes of fracture modes with decreasing stress intensities at crack tips that are often found during stress corrosion cracking and HAC of quench-and-tempered steels. It suggests that concentrated hydrogen dissolved in the lattice just ahead of the crack tip aids whatever deformation process the microstructure will allow. Intergranular, quasicleavage or microvoid coalescence fracture modes are operational depending upon the microstructure, the crack-tip stress intensity, and the concentration of hydrogen. Instead of locking dislocations in place, the model suggests that it unlocks them and allows them to multiply or to move at reduced stresses.

This model has received little support as a great deal of evidence exists to suggest that hydrogen increases the flow stress and work hardening characteristics of metals. In particular, experiments with charged nickel suggest that hydrogen decreases dislocation mobility rather than increasing it, as would be predicted by the proposed model.

194 G.J. Bieffer and M.J. Fichera of Canmet, 'Sulphide Stress Cracking Tests on Gas Transmission Linepipe' - Physical Metallurgy Research Laboratories
Report: ERF/PMRL 82-64, September, 1982

This report outlines results of Sulphide Stress Cracking tests on nine pipeline steels using the NACE standard test method TM-01-77. It reveals that consistent results using the method can be obtained on both parent and weld materials. In general, most of the parent materials showed increased threshold stresses for resistance to SSC with increasing yield strength over the range of 368-646 MPa. Weld specimens, on the other hand, were more erratic in behaviour and generally showed lower threshold stresses than corresponding parent material.

Corrosion rates were found to be quite high upon initial exposure (2000-3000 $\mu\text{m/a}$) but the rate usually decreased with continued exposure (750-100 $\mu\text{m/a}$). pH values of the depleted solutions always increased from the initial value but the final values varied considerably.

This is a valuable piece of work as it studies actual commercial alloys and not special laboratory heats. It also establishes threshold levels for cracking resistance, adding information that can be used in the design of components.

195 G.J. Biefer and M.J. Fichera of Carmet, 'Evaluation of H₂S-Induced Stepwise Cracking of Linspipe' - Physical Metallurgy Research Laboratories - Report: ERP/PMRL 83-7, February, 1983

Nine pipeline steels were subjected to Step-Wise Cracking Tests using the proposed NACE T-1F-20 procedure with two solutions, the BP Type Solution and the more aggressive NACE solution. Step-Wise Cracking was evaluated microscopically to determine the CTR, CLR and CSR of each material.

Following the discovery of SSC in some samples microhardness traverses were made across the samples. Although the macrohardness of all materials was well below the maximum Rc 22 recommended as the safe limit by NACE MR-01-75, the microhardness results indicated that every pipe contained at least one area in the heat affected zones of welds that was above the Rc 22 limit. Three pipes had numerous areas of high hardness in the parent metal, the weld fusion zone and the heat affected zone with the highest hardness being found in the HAZ.

The SWC tests revealed that under the mild BP test conditions different steels can show varying resistance. However, under the more severe NACE test condition, the steels tested were not significantly resistant. In addition, it was determined that absorbed hydrogen could not be used as an index of SWC even though the amount absorbed did increase with the amount of SWC damage.

Ultrasonic C-scan evaluation of SWC damage was shown to be effective but caution must be exercised as occasional false indications can be obtained.

An abstract of this valuable paper does not do justice to the information generated and reported. A copy of the report should be obtained and attached to this review.

196 C.A. Zapffe and C.E. Sims, 'Hydrogen Embrittlement, Internal Stress and Defects in Steel', "Transactions of the AIME", Volume 145, 1941

Hydrogen embrittlement is explained as the diffusion of hydrogen in the steel to naturally occurring voids such as non-metallic inclusions, laminations, and grain boundary triple junctions. The hydrogen precipitates in these areas as molecular hydrogen and an aerostatic pressure develops. When this pressure exceeds the yield strength of the material, fissures and blisters result. Hydrogen accumulating at the voids results in high triaxial stresses which tend to resist movement of the structure. Consequently, the application of external stress is likely to result in brittle fracture.

This article is an interesting one as it develops the theory that metals are made up of crystals that are aggregates of smaller units containing imperfections. Improvements in microscopy since the time of publication have, of course, promoted a far better understanding of hydrogen embrittlement. However, the aerostatic pressure concept is still considered as partially responsible for the phenomenon.